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## MATERIALS PROCESSING IN SPACE -- 1980 SCIENCE PLANNING DOCUMENT

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16. ABSTRACT  This report contains a detailed description of the scientific aspects of the Materials Processing in Space (MPS) program. Included are: general summaries of the possible contributions that materials science experiments in space can make to the various disciplines, rationales of why it is necessary to perform certain experiments or processes in space, a general synopsis of what has been learned from previous experiments relating to space processing, summaries of current investigations, identification of remaining issues that require resolution, and recommendations for future direction of the program.  The purposes of the report are: (1) to acquaint the reader with the overall scope of the MPS program, (2) to present the status of scientific research in the program, (3) to identify areas that may be overemphasized or underemphasized, (4) to identify critical scientific open issues in the program, and (5) to provide a basis for formulating a coherent, focused research plan.  The report is divided into six major categories: Crystal Growth; Solidification of Metals, Alloys, and Composites; Fluids and Chemical Processes; Containerless Processing, Glasses, and Refractories; Ultrahigh Vacuum Processes; and Bioprocessing. For the reader's convenience, a detailed index is provided at the beginning of each section.			
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## Preface

This document contains a detailed description of the scientific aspects of the Materials Processing in Space (MPS) program. Included are: general summaries of the possible contributions that materials science experiments in space can make to the various disciplines, rationales of why it is necessary to perform certain experiments or processes in space, a general synopsis of what has been learned from previous experiments relating to space processing, summaries of current investigations, identification of remaining issues that require resolution, and recommendations for future direction of the program.

The purposes of the document are: (1) to acquaint the reader with the overall scope of the MPS program, (2) to present the status of scientific research in the program, (3) to identify areas that may be overemphasized or underemphasized, (4) to identify critical scientific open issues in the program, and (5) to provide a basis for formulating a coherent, focused research plan.

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## Crystal Growth

### 1.0 Introduction

The possibility of using orbiting vehicles for the growth of crystals in a low gravity environment for an extended period of time offers some unique opportunities to advance the state of the art in crystal growth. These advances can come in the form of better understanding of the growth process and how it is influenced by various gravity-driven and nongravity-driven flows as well as the possibility to employ growth techniques not possible in Earth's gravity. These efforts should yield dramatic improvements in the starting material used to fabricate many electronic devices, particularly optical and infrared detectors, image arrays, VLSI circuits, nuclear detectors, microwave devices, large-scale storage devices, etc. Because of the high intrinsic values of such devices, it may become economically feasible to process the materials in space provided these processes yield sufficient gain in performance and cannot be duplicated or approximated on the ground.

This plan identifies the processes and materials for which improvements can be expected by processing in space. Also, the specific research topics required to develop the techniques of crystal growth in space into a mature technology are discussed in detail.

### 2.0 Objectives

The major objectives of the crystal growth program are to:

1. Understand the role of gravity in various crystal growth processes and determine the limitations of these processes in Earth's gravity.
2. Determine what advantages can be obtained by growing crystals in space and demonstrate these advantages.
3. Apply the findings to help solve current problems in the growth of state-of-the-art electronic and detector materials.

### 3.0 Justification

Of paramount importance in any crystal growth system is the control of the environment at the growth



interface. Compositional and/or thermal fluctuations in the fluid phase (whether it be melt, solution, or vapor) can give rise to compositional inhomogeneities or defects in the growing crystal. Since adverse thermal gradients are virtually impossible to avoid in any growth system, some convective stirring will almost always be present in conventional growth techniques. Such convective stirring is generally believed to be detrimental to the control of the growth process and is often considered to be the cause of many growth problems.

#### 4.0. Background

The types of growth that will be explored in this program are melt growth, solution growth, vapor growth, and float zone growth. These growth techniques will accommodate most of the crystals of technological interest that can benefit from suppression of gravity effects. Detailed descriptions of the current status of understanding how gravity affects such processes and the research required to establish the benefits that can be afforded by operating in a low-g environment are set forth in the following sections.

#### 4.1 Melt Growth

Crystal growth by solidification from the melt is the most widely used technique for production of high-technology, single-crystalline materials. The success of the technique depends on the control of the composition, temperature, and morphology of the solidification interface. This control is often complicated by convection in the melt which affects both the heat and mass transport to the interface. This can cause compositional variations and thermal fluctuations which, in turn, result in variations in homogeneity and growth rate.

There are several strategies available for the reduction of uncontrolled convection. Slowly lowering the sample through the heating module, as is done in Bridgman-Stockbarger growth, provides thermal stability by keeping the warmer, less dense melt above the cooler melt near the solidification region. However, in many growth systems the rejected component at the interface is less dense than the bulk fluid. As was recently shown by Coriell and Sekerka, such a system is inherently unstable even if the density gradient is favorable. This occurs because the

compositional diffusivity is much less than the thermal diffusivity. Therefore, if an element of fluid with the interfacial composition is displaced upward and allowed to equilibrate thermally, the element will be lighter, owing to its compositional differences, and will continue to rise.

Even systems without the above thermosolutal instability may exhibit gravity-dependent morphological instabilities. If a perturbation develops at the solidification interface, the composition will vary with height because of the density gradient in the melt near the interface. For example, the more dense melt that is richer in rejected solute will flow to the lowest point on the interface. This lowers the local freezing point and further retards growth at the point of slowest growth. Similarly, regions of faster growth are accelerated by the same process, leading to a morphological growth instability.

In most directional solidification configurations it is necessary to melt the sample by applying heat perpendicularly to the axis. This produces radial thermal gradients which drive convective flows irrespective of the thermal configurations in the axial direction. For non-vertical gradients, flow always results. There is no critical Rayleigh number as is the case with unstable convection. The magnitude of the flow is controlled by the Grashof number, which is proportional to the inverse square of the kinematic viscosity of the melt and cube of the critical dimension. For most materials of interest to crystal growth, the kinematic viscosity is low; therefore, the stirring from natural convection is significant, especially for the larger-diameter crystals needed for certain device applications.

One of the techniques employed to reduce the previously discussed convective flows is to apply a strong magnetic field to increase the effective viscosity. This method has been successful in suppressing convective flows in some systems but does not solve all the gravity-related problems. First of all, magnetic dampening only acts on flows perpendicular to the applied field. Also, the force that retards the flow is proportional to velocity and vanishes as the velocity goes to zero. Therefore, magnetic suppression can only slow the effect of convection and is ineffective in controlling density stratification. Finally, it can only be used with materials that are conductive.

Despite these limitations, magnetic suppression is one of the most effective techniques we have at the present for controlling convection in systems for which such control is crucial and, as such, must always be considered as an alternative to space processing of such systems. One of the major criticisms of the early MPS program was that space results were not compared against the best available ground-based techniques which would have to include magnetic convection suppression.

Two of the most important and most difficult to grow materials (HgCdTe and PbSnTe) have been selected for detailed study, and flight experiments are being developed to explore how a low-g environment might be used to overcome some of the difficulties in growing these crystals. Such materials generally have large segregation coefficients which require the buildup of high concentrations of the rejected component at the growth interface in order to obtain uniform composition in the solid. Such a diffusion layer is difficult to control, and the growth is susceptible to breakdown from constitutional supercooling and other compositional effects. In order to hope to achieve stable growth with uniform composition it is extremely important to maintain slow and precisely controlled growth conditions, free of fluctuations in growth rate. The growth interface must be held planar to prevent radial segregation and possible morphological instabilities, and a very high thermal gradient must be maintained in the axial direction to prevent constitutional supercooling. In the case of HgCdTe, additional problems exist because of the high vapor pressure of Hg which tends to upset stoichiometry as well as presenting a containment problem.

The growth problem identified with these systems placed stringent requirements on furnace capabilities and design and requires precise knowledge of the material properties, such as ternary phase information, thermal conductivity of the melt as a function of composition, diffusion coefficient, etc., in order to model the growth process and assess the thermal design.

There is reason to believe, based on Skylab experiments, that two major advantages can be realized by growing such material in space, i.e., the ability to establish a steady-state, diffusion-controlled boundary layer at the growth interface, and the ability to eliminate growth rate fluctuations. It is incumbent on the

ground-based research program supporting these two flight experiments to determine how well these problems can be controlled by alternative techniques, such as using stabilizing thermal geometries and magnetic fields to suppress the convective flows. Such experiments are also necessary to elucidate possible unforeseen problems that may be encountered in the flight experiments, and they will eventually provide state-of-the-art growth to serve as a comparison standard for the space experiments. Also, the ground-based sample will be used to develop the required characterization techniques to make meaningful comparisons between the space-grown and Earth-grown samples.

#### 4.2 Solution Growth

In many systems, an alternative to growth from the melt is growth from a saturated solution in which the solute is incorporated into the growing crystal interface. One advantage of this technique is the control it provides over the temperature of growth. This makes it possible to grow crystals that are unstable at their melting points or that exist in several forms depending on their temperature. A second advantage is the control of viscosity, thus permitting substances that tend to form glasses when cooled from their melt to be grown in crystalline form.

A number of interesting systems can be grown from transparent solutions at moderate temperature which allow the detailed study of the growth process and how it is related to growth environment. Because growth from solution requires transport of solute to the growth interface and removal of the rejected solvent, it is important to understand how the growth and perfection of the crystal are influenced by this transport process. Since the solvent virtually always has a different density from the solute, solutal-driven convection is unavoidable in terrestrial processes. In fact, forced convection or stirring is generally employed in an attempt to maintain a uniform concentration of solution throughout the growth cell.

One technique for studying the effect of forced convection on growth is to rotate the crystal through the solution so that one face is always exposed to fresh solution. It has been shown that dislocations are formed on the side facing the flux and liquid inclusions are trapped on the backside.

The various parameters which govern the growth processes and on which the origin of growth defects depends are supersaturation, temperature, pressure, nature and velocity of the solution flux, etc. These parameters are not independent and, in fact, are coupled because of the presence of gravity. In order to understand the influence of these various parameters on the generation of defects, it is necessary to be able to vary them independently. A good way to accomplish this is to perform the growth in space in order to effectively eliminate gravity-driven effects.

A number of systems have been identified as candidates for study in a low-g environment. These include:

#### 1. Tri-Glycine Sulphate (TGS)

This organic crystal is grown from aqueous solution and is very interesting from a technological point of view. It is a pyroelectric material and has great utility as an infrared detector, particularly as a room temperature detector, in the far infrared. There is a desire to improve the detectivity (d-star) of this material, which is believed to be lower than its theoretical limit by a factor of 5. It is conjectured that the performance is limited by the loss tangent which is due to microscopic inclusions in the crystalline structure. Thus, this system represents a good model material that is well characterized as well as the possibility of a technological breakthrough if substantial improvement can be realized.

#### 2. Gallium-Arsenide (GaAs)

GaAs is one of the most important III-V semiconductors, with uses ranging from microwave devices to solid state lasers. It can be readily grown in bulk form by the Czochralski method, but with considerable imperfections. Usually, in device fabrication, a thin film of high-quality GaAs with precisely controlled dopants is grown by liquid phase epitaxy (LPE) over a Czochralski-grown substrate. The LPE growth is usually accomplished by GaAs in Ga solutions.

Two problems arise. First, in the growth of the epitaxial layer, the rejected Ga solvent is less dense than the Ga/GaAs solution. Therefore, the growth system cannot be stabilized against convective overturning unless very thin liquid layers are employed in order to stay below the critical Rayleigh number. Second, it is very difficult to control the saturation at the growth interface by lowering the temperature of the substrate.

Although it is possible to bury the defects in the substrate by the thin epitaxially grown surface layer, the buried defects tend to migrate with time and eventually emerge at the surface, causing premature device degradation or failure. Therefore, for certain critical applications, it would be highly desirable to have better substrate material. For these reasons the growth of GaAs in low-g is of interest from a theoretical as well as a technological point of view.

### 3. Coprecipitation System

Another method of growing crystals in solution is by chemical coprecipitation. Two solutions are allowed to interdiffuse and react to form a precipitate with low solubility. The crystal grows by a ripening process in which the larger crystals grow at the expense of the smaller crystals in order to minimize the surface energy of the system. In terrestrial processes the crystals are often supported by a gel which also serves to inhibit convective flows. Although there are some technically interesting inorganic crystals that can be grown by this method, the primary value in the growth of such systems is to study the growth process and the relationship with defect generation. These also serve as good models for the more difficult process of growing extremely fragile organic crystals such as proteins and other macromolecular systems.

The primary interest in these crystals is to obtain structural information that relates to biological activity or other properties. To date, only a relatively small number of such crystals have been grown sufficiently large to obtain neutron diffraction data which can reveal the position of hydrogen atoms in the structure. The crystals are extremely fragile and are greatly affected by convective flows. Contamination, defects, and altered growth habit often result from the use of gels. There would be considerable research interest in such crystals if better growth methods were available.

Several attempts have been made to grow crystals from aqueous solutions in previous flights. While these produced some interesting results, the amount of control and limited measurements that were available hardly qualify these attempts as controlled experiments. For example, an experiment on the Apollo-Soyuz Test Project (ASTP) (Lind) grew three types of inorganic crystals by chemical coprecipitation. Since there was no temperature control of instrumentation associated with the experiment, it must be considered as exploratory in nature. A large number of small crystals resulted. Little could be said about the perfection of the crystals grown in low-g, although a different growth habit was observed in one of the systems.

Two additional experiments using this growth technique are planned for the Spacelab 1 payload. One experiment (Authier) is similar to Lind's ASTP experiment except that an improved growth chamber will be used and emphasis will be on determination of crystalline perfection using X-ray topography. The second experiment (Nielson) will attempt to grow the organic conductor TTF-CNQ. The facilities on the first Spacelab mission do provide better thermal control than was available on ASTP, but no measurements of the growth process or the growth environment will be obtained.

#### 4.3 Vapor Growth

There are two distinct mechanisms for growing crystals from the vapor: physical vapor deposition, in which the vapor originates from the sublimation or evaporation of the source and condenses on the seed, and chemical vapor deposition (CVD), in which a transport gas reacts chemically with the source material and deposits the material by a reversible reaction at the seed. Both are important industrial processes; physical vapor deposition is used primarily for systems that have a high vapor pressure, and chemical vapor deposition is used for the growth of refractory materials or where it is desirable to avoid the high temperature required to melt or sublimate the source material.

Generally, vapor growth does not compete favorably with other techniques such as melt growth or solution growth where large crystals are required. There are some systems, however, that do not lend themselves to other growth techniques. Also, vapor growth tends to produce

crystals with flat external surfaces and less substructure and imperfections than melt-grown crystals. Particular attention has been given in recent years to the growth of metallic whiskers and to thin monocrystalline films grown epitaxially from the vapor.

Gravity-driven convection can play an important role in the transport of the vapor from the source to seed. It is important to understand this role in order to develop appropriate control strategies. Also, the growth environment in the vicinity of the seed can be influenced by convective effects. There will be both thermal and compositional changes arising from the heat of sublimation released and from the change in concentration as the vapor deposits. These effects together with natural convection arising from temperature gradients in the growth ampoule can be expected to result in non-uniform growth conditions which would affect the morphology and perfection of the growing crystal.

Other advantages that could be expected from the study of vapor growth in space are: the avoidance of deformation of crystals that are weak at their growth temperature; the ability to grow epitaxial films under unique vacuum conditions; and the possibility of containerless growth.

Several chemical vapor growth experiments were conducted by Wiedemeier on Skylab and ASTP. The systems studied were GeSe and GeTe using  $I_2$  as the transport gas. The experiments were conducted at various pressures and in the presence of an inert gas in order to investigate the transport rates in a low-g environment. Several puzzling results were obtained. Substantial improvement in crystalline structure was obtained in terms of the surface morphology and etch pit density. The most surprising result, however, was in the transport rates.

It is generally accepted that at low pressures of the transport agent, the transport is diffusion controlled. As the pressure is increased beyond the point where transport is no longer limited by availability of carriers, the transport rate decreases because of the decreased mean free path. At still higher pressures convective flow becomes important and causes an increase in transport rate.



It was, therefore, expected that a space experiment would follow the extrapolated diffusion branch in the absence of convective flows but that higher crystalline perfection would be achieved because of the more constant growth environment. The latter result appears to have been achieved, although the characterization of the crystals that were grown in space could have been more extensive. The unexpected result was that the growth rates were substantially higher than expected, indicating that some unforeseen convective effect is operating in low-g or that some gravity-driven effect such as Clusius-Dickel-Soret transport is lowering the diffusive transport in the ground-based experiment. In either case, it is apparent that such transport is not as well understood as was previously believed.

#### 4.4 Floating Zone Growth

Floating zone crystal growth is a variation of melt growth in which the melt contacts only a like solid. This is accomplished by supporting a vertical polycrystalline rod at both ends and melting a portion of it with a suitable heater. This floating zone is supported along the sides solely by surface tension. By moving the heater or the rod, the zone can be made to move along the axis of the rod, melting the materials ahead of it and growing a crystal behind it. Often the rod is rotated or the two portions are counter-rotated to even out any thermal variations.

The primary advantages of this technique are the absence of wall effects. Many materials of practical interest are highly corrosive in the melt and will partially dissolve any container. Because the electronic properties are dramatically affected by an extremely minute trace of impurity, uncontrolled wall contamination is a serious concern. Also, the absence of wall-induced stress during the solidification process can lead to substantial improvement in crystalline perfection. For these reasons float zone growth is an extremely important process, especially for producing high-quality silicon and other electronic materials for applications in which high purity and perfection are required.

Floating zone growth is subjected not only to the control and stability problems at the interface that are encountered by ordinary melt growth, but has also a new set of problems associated with the free surface. Because

the hydrostatic pressure in the zone must be supported by surface tension, the length of the zone is limited by the material properties and the diameter of the system. For some materials, the allowed zone length becomes so short that it is not possible to establish the desired thermal profiles at the growth interface. Also, the sagging of the melt under the hydrostatic pressure further complicates the control of the meniscus at the growth interface and, consequently, the size and shape of the growing crystal. In addition, the thermal convection in the melt is further complicated by surface tension-driven flows (Marangoni convection) arising from variation of surface tension with temperature along the free surface of the melt.

Float zone crystal growth would apparently benefit significantly from the low-g environment in space. The absence of hydrostatic head eliminates the deformation of sag of the molten zone. Zone lengths may be increased to the length imposed by the Rayleigh criteria for stability (length equals the circumference). Finally, the use of low-g processing extends floating zone growth to materials whose low surface tension prohibits this technique on Earth.

## 5.0 Experiment Status and Remaining Issues

### 5.1 Melt Growth

From the preceding discussion it is apparent that the role of gravity in the growth of crystals from the melt is very complex and not completely understood. Obviously, the available techniques are quite adequate for many or most device applications, as the thriving electronic industry will attest. There is a demand, however, for improved materials for certain applications, such as infrared detectors. The philosophy of the MPS crystal growth program is to focus on understanding the effects of gravity in these processes in order to devise better control strategies, identify gravity-related limitations, and demonstrate that these limitations can be overcome by space processing.

#### 5.1.1 Growth of Solid Solution Semiconductors in Space (Davidson)

The objective of this experiment is to produce high-quality, solid-solution, alloy-type semiconductors for use as infrared detectors or as IR transparent substrates

on which IR detectors can be grown by LPE or other techniques. Emphasis has been given to  $\text{Hg}_{.8}\text{Cd}_{.2}\text{Te}$  because of its importance as a detector material and because it is generally accepted as one of the most difficult materials of this type to grow on Earth. One of the major goals is to achieve a very low intrinsic carrier concentration in order to extend the bandwidth from the existing 2 GHz to approximately 5 GHz in order to satisfy a Department of Defense (DOD) requirement.

First priority was given to the ampoule design. Since the vapor pressure of Hg at the liquidus temperature is  $\sim 100$  atmospheres, this is not a trivial problem. Quartz has been found to be satisfactory, provided adequate sample purity is maintained. Elaborate purification techniques have been developed in which the growth ampoules are filled by a distillation process.

Several conventional growth techniques have been carried out in the laboratory to understand their limitations and to obtain samples to compare with commercially available material. These ground-based techniques include quench-anneal, traveling solvent, and Bridgman-Stockbarger. The latter has yielded small diameter single crystals comparable to the best commercially available material; however, the composition varies by as much as 20 percent over the sample because of uncontrolled convection and interface morphological instabilities. Because the  $\text{HgTe}$ -rich diffusion interface is more dense than the average melt, this system is subject to the gravity-dependent interface instability described in Section 4.1.

Of particular importance in designing the space experiment is obtaining sufficient thermal gradient to prevent constitutional supercooling and interfacial breakdown. This requires detailed knowledge of the phase diagram and accurate values for the diffusion coefficient. Considerable effort has gone into the latter; however, it is difficult to obtain accurate values because of the high vapor pressures involved.

#### 5.1.2 Growth of $\text{PbSnTe}$ in Space (Crouch)

This experiment is similar to the Davidson experiment described previously except that the material of interest is  $\text{PbSnTe}$ . This material has many of the problems inherent in the  $\text{HgCdTe}$  system except that the vapor

pressure is considerably lower at the liquidus temperature. Also, the rejected component is less dense than the average melt; therefore, the system is subject to thermosolutal convection, as discussed in Section 4.1.

#### 5.1.3 Growth of Solid Solution Ternary Systems (Lehoczky)

This effort supplements the Davidson work on HgCdTe by providing fundamental data on the system, such as obtaining a more accurate pseudo-binary phase diagram, investigating portions of the ternary phase diagram, measuring the vapor pressure as a function of temperature above various compositions of HgCdTe, measuring diffusion coefficients as a function of composition, and developing theoretical models relating electrical properties to crystalline perfection.

#### 5.1.4 Defect Chemistry of HgCdTe (Vydynath)

This study is an attempt to analyze and predict the defect density in HgCdTe from first principal statistical mechanical arguments. The predictions compare favorably with measured defects in crystals grown by quench anneal.

#### 5.1.5 Interfacial Stability Criteria (Tiller)

The theoretical aspect of this study is a reexamination of the criteria for the gradient-to-growth (G/R) ratio at a growth interface required to maintain interfacial stability in light of the solid state diffusion of the high solute concentration at the melt interface. An experimental apparatus using a transparent furnace with transparent model systems has been developed to investigate these effects on the ground.

#### 5.1.6 Growth of III-IV Semiconductors (Gertner)

The original objective was the growth of III-IV solid solution infrared detector substrates with a large band gap and an adjustable lattice parameter. This lattice parameter can be adjusted by choosing the proper composition to match the LPE-grown electrical active layer. Because the wide band-gap substrate is transparent to infrared radiation, the countercurrent distribution (CCD) readout circuitry can be placed directly on top of the detector array.

Recent advances in matching lattice parameters by step grading and linear grading have obviated the need for growing solid solution substrates with controlled lattice parameters. Therefore, the emphasis has been shifted to growth of CdTe.

#### 5.1.7 Remaining Issues

1. The appropriate criteria for interfacial stability must be reconsidered, particularly for systems in which the rejected component is more dense than the bulk melt. The stability of such systems in low-g must be assessed.

2. The limitations imposed by thermosolutal convection on various melt growth processes should be assessed. The possibility of zone melting as an alternative should be considered.

3. The effectiveness of magnetic damping in stabilizing these systems must be determined.

#### 5.2 Solution Growth

##### 5.2.1 Growth of TGS in Zero-g (Lal)

A unique technique has been developed to grow crystals from aqueous solution in low-g. Instead of slowly increasing the saturation by lowering the temperature of the bath, as is done in conventional solution growth, the walls are kept isothermal and the crystal temperature is slowly lowered by extracting heat through a specially cooled sting. In this manner saturation conditions can be met at the growth interface even though the concentration is lower at the crystal than anywhere else in the solution, a condition imposed by diffusion-controlled growth conditions. Holographic data and thermistors will provide information on the growth environment. The experiment will be performed in the Fluids Experiment System (FES) of Spacelab 3.

Complete characterization of the growth solution has been accomplished. A number of crystals have been grown in a simulated FES test cell, but without the cooled sting. Characterization techniques are being worked out.

### **5.2.2     Liquid Phase Epitaxy of GaAs (Lind)**

An experiment was flown on Space Processing Applications Rocket V (SPAR V) to evaluate the growth of GaAs by LPE in low-g. In Earth's gravity the system is unstable against thermosolutal convection (as described in Section 5.1.5 of Solidification of Metals, Alloys, and Composites), requiring the melt to be restricted in depth to stay below the critical solutal Rayleigh number.

The flight was successful, and the growth obtained is being analyzed.

### **5.2.3     Electro-Epitaxial Growth of GaAs (Gatos)**

A unique technique has been developed for the isothermal growth of epitaxial layers of GaAs by passing a current through the melt and collecting it at the substrate. The As migrates by electron transport to the growth interface, thus maintaining saturation conditions. The heat of solidification is removed by Peltier cooling at the solid-liquid junction. This allows much more control over the growth than is possible by conventional LPE techniques.

High-quality layers of GaAs have been grown over GaAs substrates using this technique. Growth rates are very limited on Earth because of the Joule heating effects which can cause uncontrolled convection; therefore, the process is only applicable to thin films on Earth. In space it may be possible to grow defect-free GaAs substrates by this method.

### **5.2.4     Crystal Growth by Coprecipitation**

There is currently no MPS-sponsored program in this discipline.

### **5.2.5     Remaining Issues**

1. Use of the cooled-sting technique should be examined for growth of technologically important crystals such as Urea and KPB, which are very difficult to grow by conventional solution growth techniques.

2. There is concern as to whether a TGS crystal of sufficient size can be grown in the time available on Spacelab to evaluate the effects of low-g growth. How can one distinguish the low-g growth from the seed? Will seed effects propagate into the new growth?

3. The advantages of growing delicate macromolecular crystals in space should be explored for the purpose of obtaining structural information. What pertinent experiments are required to answer this? Could such crystals be returned without damage? Would it be feasible to do the analysis in space?

### 5.3 Vapor Growth

#### 5.3.1 Vapor Growth of Alloy-Type Semiconductors (Wiedemeier)

Extensive analysis has been performed together with additional ground-based experiments to clarify the anomalous growth rates observed with the GeTe and GeSe systems flown on Skylab and ASTP. Growth rates measured as a function of pressure and ampoule orientation confirmed that the rates observed in spaceflight experiments lie well above the diffusion branch, indicating that something unusual is happening. Several new systems are being prepared for flight on the Shuttle; i.e., HgCdTe and CuInSb. Suitable transport gases have been identified and the reaction rates have been determined. Growth of the systems in the laboratory has been accomplished, and characterization techniques are being developed. An additional experiment is being planned to help elucidate the anomalous transport rates discussed previously. This will not use a chemical transport agent but will consist of sublimation in the presence of an inert gas. This will determine whether or not chemical reactions and the heat released in the transport channel are responsible for the flows that produce the higher transport rates.

#### 5.3.2 Growth of HgI<sub>2</sub> in Space (Schnepple)

The motivation in this experiment is to obtain improved performance of HgI<sub>2</sub> as a nuclear detector material by improved perfection. One of the factors that is believed to limit the performance of this material is the extreme weakness of the crystal at the growth temperature. Because the crystal has a layered structure with only van der Waals forces bonding the layers together,

self-deformation during growth under one-g is believed to be an important factor in producing dislocations which limit the carrier lifetime and degrade the performance as a nuclear detector. The growth of such a crystal in low-g could in principle eliminate such strains at the growth temperature. It is also anticipated that the perfection of the crystal might benefit from the more quiescent growth conditions expected in space.

#### 5.3.3 Fluid Dynamics of Crystal Growth (Rosenberger)

An extensive study of the fluid dynamics of vapor growth is being sponsored by NASA, National Science Foundation (NSF), and Department of Energy (DOE). As part of this effort a two-dimensional, axis-symmetric, convective-diffusive transport model of the vapor growth process has been modeled. Analyses of the thermo-concentration stability have been carried out.

These studies have been applied to the Schnepfle HgI<sub>2</sub> experiment to determine the degree to which convection affects the transport and growth morphology in order to determine how much change one might expect in low-g growth.

#### 5.3.4 Vapor Growth of PbSnTe (Zoutendyk)

This effort consists of various studies of the effects of gravity-driven convection in the growth of PbSnTe from the vapor as a definition study for a possible flight experiment.

#### 5.3.5 Remaining Issues

1. The anomalous transport rates observed by Wiedemeier have still not been resolved, and their importance to the fundamental understanding of the transport process remains unclear. A critical experiment is required to establish whether these are related to chemical reactions in the transport gas, as suggested by Wiedemeier; removal of possible gravity-related reverse transport processes, as suggested by Rosenberger; or some artifact of low-g-related convective flows of the transport gas or motion of the seed crystals in the growth ampoule.



2. The rationale for vapor growth in low-g is not well established. Fluid dynamical considerations suggest that gravity-driven convection is not a dominant process even in unit gravity, although its presence may still produce unwanted fluctuations in growth.

3. The importance of gravity-related strain in producing growth defects in  $\text{HgI}_2$  has not been established. Also, it is not clear that a sufficiently large crystal can be grown in the time available in space to demonstrate the possible advantage of low-g growth of this material.

#### 5.4 Float Zone Crystal Growth

There are no floating zone experiments presently approved for flight, but there is an active working group that is developing a group of experiments to be accomplished on the Analytical Float Zone Experiment System (AFZES), which is under definition study.

##### 5.4.1 Marangoni Flow in Float Zone Crystal Growth (Fowle)

A conceptual design of an AFZES has been developed which consists of temperature and surface velocity measurements, zone morphology, interface demarcation by Peltier pulsing, and in situ surface analysis. This facility would be used to study the float zone growth of Ga, Ge, and eventually Si in low-g and assess the importance of Marangoni (surface tension-driven) flows on the heat and mass transfer. If such flows can be controlled, the longer zone length allowed in space offers the possibility of flatter, better controlled interfaces that should greatly improve the problem of radial segregation.

A horizontal boat with built-in heaters to establish a uniform gradient has been constructed to begin making surface measurements and assessments of Marangoni flows.

##### 5.4.2 Marangoni Convection (Ostrach)

This effort is directed toward obtaining analytical scaling laws and computer models of the surface and deep-level flows arising from surface tension in a floating zone. Appropriate dimensionless parameters and length scales have been identified. A solution has been obtained for the flow in a thin infinite sheet heated

along a line. This can be approximated experimentally and checked. Deep-layer flows will require the addition of the nonlinear inertial terms.

5.4.3 Computer Models of Marangoni Convection in a Floating Zone (Brown)

See chapter on Fluids and Chemical Processes.

5.4.4 A Study of Surface Tension Flows (Davis)

See chapter on Fluids and Chemical Processes.

5.4.5 Development of a Laser Doppler Velocimeter for Surface Measurement (Mann)

Two powerful techniques for surface analysis have been developed using laser Doppler velocimetry (LDV). In one case laser beam scattering from the ripples (statistical fluctuations of the surface) is autocorrelated. The Fourier transform of the autocorrelation can be interpreted in terms of local surface temperature, modulus of elasticity, surface tension, and surface velocity.

The second technique uses a beam splitter to form two beams which are imaged at the same point on the surface. The reflections of these two beams are combined in an interferometer and autocorrelated. Again, the Fourier transform of the autocorrelation function is a sensitive measure of surface velocity. It has been shown that the latter method works from the scattering of small impurities on the surface.

5.4.6 Effect of Surface Active Impurities on Marangoni Flow (Verhoeven)

An ultrahigh vacuum system has been assembled to perform a number of experiments assessing the role of surface films, such as oxide layers, in inhibiting Marangoni flow in a floating zone configuration. A controlled leak can admit precise amounts of oxygen or other gas. Surface layers can be measured in situ by Auger depth profiling and later by a sputter ion mass spectrometer (SIMS).

First experiments will be performed on Sn zones supported on the inside by a thin stainless steel tube to help stabilize the zone. Later tests will be run using

Ge zones. The Marangoni flow will be measured as a function of oxide layer thickness to determine the effectiveness of such layers in controlling Marangoni flows.

#### 5.1.7 Remaining Issues

There are two basic issues involved:

1. What is the magnitude of the Marangoni flow, and how is it influenced by surface effects?
2. What does the flow do to the process, particularly to the region near the interface?

Secondary issues center around the techniques and approach being used; i.e.:

1. It may be more efficient to measure the effects of surface films on surface tension-driven flows by using Ostrach's horizontal pool technique than by using an actual float zone configuration.
2. Surface tension and how it varies with contaminants is strongly a function of material. It would, therefore appear more meaningful to work with actual candidate materials for float zone processing in space rather than model materials such as Sn, Ga, or even Ge.
3. There may be an overemphasis on the analysis of the bulk flows when the driving forces are not yet known. More attention should be given to the boundary layer at the solidification interface. This, after all, is what determines the quality of the crystal that can be grown.

#### 6.0 Assessment and Recommendations

The crystal growth program is the most mature and, consequently, the strongest MPS program, both scientifically and technologically. There is a good chance that significant contributions will be made by space experiments, and it is not unrealistic to expect space manufacturing of certain materials to be economically viable.

One of the primary beneficiaries of this program is DOD. Efforts by Systems Planning Corporation (SPC) to acquaint the DOD with the MPS program have revealed the following:

1. Relatively little effort goes into basic materials research. The bulk of the research is devoted to device fabrication.

2. The size of the NASA program in MPS is so small compared to other research efforts that it is generally discounted as too insignificant to be concerned with.

3. We have not proved our case by producing substantially better material in space or by developing convincing arguments that show that gravity effects are the limiting factor in certain processes.

The thrust of the crystal growth program should be directed toward answering the preceding item 3.

#### 6.1 Melt Growth

The two flight experiments together with the supporting research efforts represent a fairly complete research team of outstanding investigators that should produce some exciting results. Davidson appears to have discovered a gravity-dependent interfacial destabilizing mechanism that had not been considered previously. The mechanism becomes important when the rejected component is more dense than the bulk melt. This, with the work of Coriell and Sekerka that demonstrates the instability of systems in which the rejected component is less dense than the bulk melt, essentially means that all systems are inherently unstable in a gravitational field. This may be the most compelling argument for the growth of crystals in space.

Additional work on this effect is urgently needed in the form of a complete mathematical stability analysis. Although, intuitively, the interface appears to be morphologically unstable, the process appears to be limited by the thermal gradient. The extent of the macro-segregation produced by this effect should be calculated. This should be supplemented by experiments with transparent model systems on the ground and in space demonstrating this instability.

#### 6.2 Solution Growth

The TGS experiment of Lal and Kroes is a well-conceived experiment that offers an innovative method

for solution growth. There is concern, however, that a sufficient amount of crystal to do a meaningful characterization can be grown in the time available. Consideration should be given to strengthening this team with some leading experts in solution growth, characterization and industrial users of TGS.

The principal value of this experiment may very well lie not with TGS but with other systems that are difficult to grow by conventional techniques. Examples are Urea and KPB. These optically active crystals can serve as frequency doublers in the ultraviolet. However, attempts to grow these materials by conventional methods result in dissolution of the seed and a fine precipitate. Such systems may quite possibly be grown by the cooled-sting technique. Macromolecular crystals, important for biological systems (see chapter on Bioprocessing, Section 6.6), could also possibly be grown by these techniques.

The GaAs effort of Gatos also appears to be an outstanding scientific and technical piece of work with excellent commercial possibilities. Consummation of a joint endeavor to develop this process for space manufacturing would be a major milestone in establishing the commercial viability of growing crystals in space.

Finally, since the FES is ideally suited to the study of solution growth on the ground as well as in space, additional experiments should be developed for this facility. At the Fluids Experiment System Workshop held at Marshall Space Flight Center (MSFC) in July 1979, nine crystal growth experiments were identified that could benefit from use of this facility. The interest from the scientific community is there. What is lacking is the availability of early flight opportunities.

### 6.3 Vapor Growth

The group of investigators involved in vapor growth is modest in number but is of exceptional quality. All of the basic elements are represented: an excellent experimentalist (Wiedemeier), an excellent theorist (Rosenberger), and an industrial user (EG&G). An interesting scientific controversy has developed; i.e., the interpretation of the apparently anomalous transport rates observed by Wiedemeier on early flights. This should serve to stimulate scientific interest.

Wiedemeier's experiment is primarily aimed at the growth of potentially useful materials (HgCdTe and CuInSb). While this is desirable, the complexities of these systems are such that these experiments will do little to resolve the anomalous growth problem mentioned earlier. It is important, therefore, that consideration be given to flying a simplified physical vapor transport ampoule on the Materials Experiment Assembly (MEA) to establish whether the enhanced transport observed on previous experiments is actually caused by chemical reactions or whether it is a physical effect. This effort should be strongly encouraged. In addition, ground-based work on chemical profiling the transport tube, using laser Raman or mass spectrometer techniques, should be encouraged.

The EG&G effort to grow HgI<sub>2</sub> in space is an interesting experiment from a technical point of view. However, there is concern that the crystal grown in space in the time available may not be large enough to exhibit the benefits that are hoped to be achieved by growth in a low-g environment; i.e., lack of defects produced by hydrostatic strain deformations. Also, it has not been established that gravitational strain is the primary cause of such defects. Thermal cycling and the strain induced by the support mechanism because of differential expansion could well be the dominant factors. Additional work is needed to develop a clear rationale for this experiment.

One potential advantage that could be realized in space (and to a limited extent on the ground) is the possibility of vapor growth without contact of the seed. This could eliminate one of the major causes of defects; i.e., induced strain because of the physical contact with some support mechanism. Preliminary experiments with an acoustic levitator have demonstrated that ice crystals can be grown containerlessly by suspension in an acoustic well. It would be relatively simple to extend this technique to HgI<sub>2</sub> since the growth temperatures are modest.

#### 6.4 Float Zone Growth

An excellent team of scientists has been assembled to develop concepts for an Analytical Float Zone Experiment System which would explore the advantages and problems of float zone crystal growth in space. Although the scientific credentials of this team are impeccable, what seems to be lacking is a close tie with potential users of a space-borne float zone facility. Therefore, one questions if

the effort is really directed toward solving the most essential problems.

Unfortunately, the power limitations imposed by Spacelab apparently preclude the growth of Si, which is the material of greatest interest to the industrial community. The major emphasis of the APZES appears to be the study of the Marangoni convection in the floating zone. Such flows are completely dependent on the surface active contaminants. It appears that such behavior is highly dependent on the material in question. Therefore, it is not clear that such studies on Su, Ga, or Ge really apply to Si. Surface tension variations and Marangoni flow can certainly be measured on the ground. Emphasis should be given to such measurements for Si and other potential float zone materials such as InSb, CdTe, etc. At present four investigations on studying and modeling flows are being sponsored by the MPS program. Because such flows are generally detrimental and tend to negate the advantages of going to space, it is important to develop methods for control or suppression of such flows. More emphasis should be placed on the investigation of effects of surface active contaminants, oxide layers, or liquid encapsulants on the materials of interest to see if the driving forces can be diminished or eliminated.

The thermal profiles from the heating and heat extraction system are of paramount importance in establishing and maintaining a flat growth interface and should be systematically investigated. The avoidance of compositional inhomogeneities or radial segregation is one of the major advantages of float zone growth in space. Another major concern is the control of materials that have high vapor pressures, which is the case for many potentially interesting systems. Can this be controlled by the use of surface active contaminants or by liquid encapsulants? Consideration should also be given to the use of unconventional floating zone geometries that cannot be used in unit gravity but that could provide much higher thermal gradients and better interfacial temperature control.

The LDV system developed by Mann promises to be a major breakthrough in surface measurement technology. This technique should be developed for use in conjunction with ground-based studies on the effects of various surface films for control of surface tension-driven flows.

Considerable work with transparent model systems can be done on the ground, as evidenced by the work of Schwabe and others in Germany. A flight experiment on Spacelab 1 is being planned by deRiva. These efforts should be examined carefully before flight experiments with model systems are planned.

#### **6.5      Supporting Research Required**

For the success of crystal growth from the melt, the major key is precise temperature control at the growth interface. For most applications this also requires : very high gradient in the melt at the interface. Emphasis has been directed in previous years to the development of high temperature heat pipes for use as furnace liners in order to obtain the highest possible gradient.

The biggest factor in obtaining high gradients in a sample is the coupling efficiency between the sample and the heat source and heat extractor, particularly on the cold end where radiation transport is inefficient. The largest gain in high gradient furnaces of conventional (cylindrical sample) geometry can be made by improving this low temperature heat extraction, perhaps by use of liquid metal in conjunction with a medium-temperature heat pipe. A heat pipe on the hot end does not appear to offer any real advantage. In fact, higher gradients can be achieved by a nonuniform axial temperature profile.

The maximum gradient that can be obtained in a cylindrical sample is limited by the maximum temperature above the solidus temperature that can be withstood by the ampoule. The only way this can be improved is to go to different sample geometries, such as a planar geometry for the melt with material fed in from the sides (Flemings' concept). Such concepts should be explored in more detail, especially for materials with high vapor pressure.

#### **6.6      Working Group Activities**

At present there are essentially two working group activities supporting the crystal growth program. Both groups are composed essentially of the investigators under contract. These groups need to be expanded to include more potential users; i.e., DOD contracts and industrial crystal growers. Consideration should be given to the establishment of a single working group devoted to MPS crystal growth, with each of the major disciplines forming subgroups.



## SOLIDIFICATION OF METALS, ALLOYS, AND COMPOSITES

## Solidification of Metals, Alloys, and Composites

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## Solidification of Metals, Alloys, and Composites

### 1.0 Introduction

Control of the solidification of metals and alloys is the key element in the vast field of metallurgy which provides us with the materials that are fundamental to our high technological society. Gravitational effects such as buoyancy-driven convection of the melt or the sedimentation of various phases can greatly influence the macrostructure as well as the microstructure of metals and alloys. Some of the effects are beneficial, such as the removal of bubbles, whereas other effects give rise to difficulties such as phase separation, freckling, or inhomogeneous composition. Some of these effects are subtle and are only now beginning to be appreciated.

### 2.0 Objectives

The objectives of the study of gravitational effects on the solidification of metal and alloys are to (1) identify various aspects of the field of solidification phenomena that may be affected by gravity-driven flow, (2) devise and conduct critical experiments in both increased gravity as well as in space to elucidate these effects, and (3) impact the field of metallurgy by contributing fundamental knowledge to the field of solidification by devising better control strategies to eliminate the undesirable effects of gravity and/or by producing exemplary samples of material to establish the benefits of better control of the solidification.

### 3.0 Justification

Because of the relatively low cost and large volume of metals required by our society, the routine production of such metal products in space does not appear to be economically justifiable, although it is not inconceivable that some highly specialized products may have sufficient value to recover the high transportation cost. For this reason, space experiments are regarded as a means of solving problems by using this unique environment to eliminate certain undesirable gravitation effects. Because of the large volume of material involved and the impetus to develop improved materials for future technologies, the value of research to improve the control of the solidification process is great. Because space offers

a unique opportunity to eliminate one of the major factors which can provide disturbing influences in the control of the solidification process, such research may prove to be the most economical, if not the only, means of investigating such effects. Already a number of industries have expressed an interest in participating in this type of research.

#### 4.0 Background

The solidification of a multicomponent metallic system is a highly complicated process. After the first-to-freeze component nucleates and begins to grow, the composition ahead of the solidification front begins to change dramatically because of the segregation coefficients of these components. For systems containing more than two or three components, the phase diagram becomes extremely complicated and is usually not known. Often uncontrolled thermosolutal convection results because of thermal as well as compositional gradients. This results in continuously changing compositions as the solidification proceeds. The science of metallurgy continually strives to control these processes in order to obtain various microstructures that determine the physical properties of the metal.

#### 4.1 Casting of Alloys and Composites

In many cases it is unfeasible or undesirable to provide sufficient gradients to maintain a planar solidification front as is done in crystal growth from the melt. Therefore, dendritic growth results. The interdendritic fluid, which has a different composition from the solidifying material, often becomes trapped in the spacings between the dendrites, which results in a varying microstructure. Dendrite arms break off either because of ripening effects, convective flows, or the expulsion of the interdendritic fluid as the growth proceeds. They are carried by density differences or by convective flows and either form nucleation sites for new growth or migrate to the surface and produce freckles. The multiplication of nucleation sites by this process is responsible for producing the fine-grain, equiaxed structure in the interior of a casting, as was recently shown by a series of varying gravity environments using a centrifuge.

Even simple congruently melting systems, such as Al-Sb that forms a compound directly from the melt, show surprising gravitational effects in solidification. In an ASTP experiment in which great care was taken to maintain stoichiometry, the ground control sample contained a significant amount of the noncompound phase with an Al-rich region at the bottom and an Sb-rich region at the top. The space-processed sample showed almost complete formation of the compound. Apparently small fluctuations away from stoichiometry are intensified by differences in density, allowing the denser fluid to become displaced before it can re-equilibrate by diffusion. It may also be possible that there is density stratification even in a single liquid phase because of clustering effects between like atoms. Such effects have been seen at high-g even in systems that are completely miscible but do not behave as ideal solutions. There may be some subtle effects from such behavior even in unit gravity.

At one time it was believed that a low-g environment might offer ideal opportunities for preparing various composites and/or foams. Some early space experiments attempted to suspend second phase particles in a melt with the hope that the lack of buoyancy would permit the achievement of uniform distributions.

The results for the most part were disappointing. In some experiments the second phase particles were not uniformly distributed, and often bubbles or voids permeated the casting. Even where fairly uniform distributions were achieved, the physical properties did not appear to be enhanced to a degree that would justify the expense of processing in space. Also, present materials technology has succeeded in making a variety of composites by powder metallurgy techniques, aligned fiber techniques, and various other methods. Many problems remain, such as obtaining good dispersions of extremely fine particles for dispersion hardening or for the preparation of solid electrolytes. However, the particles of interest for these applications are generally below a micron and are not affected by gravitational sedimentation.<sup>1</sup>

For these reasons it appears that low-g experimentation should concentrate on the more fundamental problems involved in the formation of composites rather

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1. They are kept in suspension by Brownian motion.

than attempt to actually make superior composite material in space.

#### 4.2 Directional Solidification

Special highly anisotropic microstructures can be obtained with some systems by directional solidification. This technique affords a degree of control not available in normal castings in that a unidirectional thermal gradient can be imposed on the sample and the growth rate can be regulated by moving the sample relative to the thermal gradient. Convective effects can be diminished by the application of stabilizing thermal gradients and magnetic fields to the limitations imposed by thermosolutal stability, radial gradients, and magnetic viscosity.

Directional solidification is often used to produce in situ composites with regular structure of materials whose components have limited solid state solubility. The size and spacing of the microstructure is determined by the growth rate, the higher growth rates giving rise to finer microstructures. These higher growth rates require very high thermal gradients to control the interface and prevent it from breaking down. For this reason there has been considerable effort in developing techniques for producing very high gradients. Low-g offers several possible advantages. First, the reduced convection in the melt lowers the Nusselt number (the ratio of total heat transfer to conductive heat transfer) to unity. Because the maximum thermal gradient that can be imposed on the molten side of a solidification interface is diminished by increasing the effective conductivity of the liquid, it should be possible to obtain higher gradients in low-g (all other things being equal). Second, shapes can be maintained in low-g with a thin oxide skin, as was demonstrated in experiments performed on Texus I and II. This allows complicated shapes, such as turbine blades, to be melted and directionally resolidified using a thin oxide skin to maintain the shape. Without the heavy mold required on Earth to diffuse the heat, a very high thermal gradient can be imposed on the sample which can produce a unique, very fine microstructure.

Diffusion effects are believed to control the cooperative growth of eutectics by directional solidification. Uncontrolled convection can certainly disrupt the growth process unless care is taken to reduce its effects.

For reasons discussed previously, it is not possible to eliminate convective flows completely in Earth's gravity. Low-g experiments on Mn-Bi/Bi eutectics have shown improved microstructures in terms of uniformity of rod size and spacing over what could be obtained on the ground. There are some indications from these experiments that uncontrolled convection may play a greater role in such growth processes than previously expected.

Another advantage of low-g lies in the processing of off-eutectic compositions. By eliminating the convective stirring associated with one-g processing, it is possible to build up a diffusion layer of the rejected component until the eutectic composition is reached at the interface. To provide mass balance, however, it is necessary at steady state to incorporate the same net composition into the solid as is present in the bulk melt. This results in both alpha and beta phases solidifying but in proportions determined by the bulk melt composition. This provides a new degree of freedom in controlling the size, shape, and spacing of the two phases.

#### 4.3 Monotectic Alloys

Monotectic alloys are another important class of materials that require reduced gravity for detailed study. These alloys are characterized by a region of immiscibility in the liquid phase diagram. Attempts to form alloys or fine dispersions of such material in Earth gravity by normal freezing are doomed to fail because of this immiscibility gap. As the melt is lowered below the consolute temperature into the two-phase region, the minority phase nucleates and forms droplets in the majority phase. Because these two phases invariably have different densities, they will rapidly separate as the droplets grow by diffusion to sizes of a few microns. The result is an almost complete stratification of the two metals.

Such miscibility gap alloys can be formed by rapid solidification techniques such as splat cooling or melt spinning, but these methods do not lend themselves to preparing bulk samples. Solid or powder metallurgy techniques employing liquid phase sintering and hot isostatic pressing are the only techniques available for preparing such materials which have found numerous applications in electrical contact materials, turbine blades, and various high-temperature alloys. However, such techniques do not



achieve the intimate contact between the two phases that would be possible if the composite were prepared from the melt. How this would affect the mechanical and electrical properties of the materials is not known, although fine dispersions of Ga-Bi prepared in a drop tower did show some unique electrical properties.

A number of attempts have been made to prepare fine dispersions of monotectic alloys in space. These have generally been unsuccessful for reasons that are not well understood. It was believed that the absence of sedimentation would allow the fine dispersion, which forms when cooling the melt through the two-phase region, to be solidified in place. Indeed, this was demonstrated in the GaBi experiment in the drop tower. However, it is now becoming apparent that there are nongravitational effects that produce massive separation of the phases. It is clear that the system is somehow driven to a configuration that minimizes the total interfacial energy when solidified under low-g. What is not clear are the mechanisms that give rise to the flows. The study of these effects is important from a fundamental point of view as well as to determine how to prevent such separations.

#### 4.4 Nucleation and Growth in Undercooled Melts

Nucleation and rapid solidification of deeply undercooled melts are other important phenomena that are of fundamental as well as practical interest. By containerless melting and solidification, wall-induced nucleation can be eliminated. This allows the melt to be cooled substantially below the normal freezing point before homogeneous nucleation eventually occurs. Solidification under these conditions is extremely rapid and can produce unique microstructures, metastable phases, or amorphous solids. These structures are thought to be similar to those produced by rapid quenching of thin samples by splat cooling, except the bulk sample can be processed.

One particular application is the production of bulk samples of superconducting A-15 compounds such as  $\text{Nb}_3\text{Ge}$  and  $\text{Nb}_3\text{Sn}$ . By producing these compounds in samples large enough to analyze by neutron diffraction, the relationship between perfection of the crystalline structures and the superconducting performance can be analyzed. Such studies may shed some light on methods for obtaining higher transition temperatures.

## 5.0 Experiment Status and Remaining Issues

### 5.1 Casting of Alloys and Composites

#### 5.1.1 Casting Experiments (Johnston)

This effort is an extension of earlier SPAR experiments, which used transparent model systems to investigate the gravitational influence on the solidification process, to actual metallic systems. Effects such as macrosegregation and microsegregation, grain size, shape, and orientation, and physical properties of ingots cast in low-g will be compared to identical castings in unit-g and higher-g environments. A striking decrease in grain size with increasing g-field has already been demonstrated, confirming earlier predictions that dendrite multiplication is influenced by gravity-driven convective flows.

A casting furnace has been completed and flown on SPAR VII. This will be complemented by additional rapid-quench casting experiments carried out in KC-135 aircraft. A special furnace for this purpose has been constructed and is being tested for use beginning in mid CY 1980. Additional experiments could also be carried out in the drop tower when it is reactivated in mid CY 1980.

#### 5.1.2 Study of Dendritic Growth at Low Undercooling (Glicksman)

The objective of this study is to elucidate the gravitational effects in the growth of dendrites at low undercooling, where convective flows begin to become important in heat transport. Theoretical analysis, confirmed by experimental measurements, accurately predicts the growth rates for large undercoolings where diffusive transport dominates. A departure from this theory as well as a shape distortion of the side branches has been observed at low undercooling, indicating the onset of gravitational influences.

#### 5.1.3 Particle Pushing by Solidification Interfaces (Uhlmann)

When a solidification interface encounters a second phase particle, there is a tendency for the particle to be pushed ahead by the so-called disjoining pressure that results from the long-range intermolecular

forces (Lifshitz forces). When the drag forces overcome the disjoining pressure, the particle is engulfed by the solidification front. Such effects may be important in the casting of composites containing fine dispersions of second phase particles. A theory has been developed relating the critical velocity where a particle is engulfed to the size and thermal properties of the particle and the Hamaker constant.

A critical experiment was carried out on SPAR V to provide experimental confirmation of the theory.

#### 5.1.4 Foam Metals (Pond)

In principle, one should be able to prepare a closed-cell foam metal in the absence of buoyancy forces, although there are questions about the stability of such a foam because of surface tension effects. An attempt to form such a foam will be made on SPAR VIII. A mixture of powdered Cu and graphite will be heated above the melting point of Cu. The graphite will react with the oxide on the Cu particles and act as a blowing agent. The objective of the experiment is to determine if a stable foam will form and to investigate the parameters that control the number and size distribution of the cells.

#### 5.1.5 Thermosolutal Convection (Coriell)

It is well known that, since most fluids expand when heated, a configuration with a vertical thermal gradient (hot above cold) is stable against convection. This is an important strategem for reducing unwanted convection in many solidification processes. However, in the solidification of multicomponent systems a compositional gradient will build up in the melt because of the partial rejection of one or more of the components by the solid. This study investigated the stability of such systems with combined thermal and solutal gradients.

It was found that systems with inverted concentration gradients were unstable even with an overcompensating thermal gradient such that the overall density decreases with height. This somewhat surprising effect results from the fact that mass diffusion is several orders of magnitude lower than thermal diffusion. Therefore, an element of fluid displaced upward will come to thermal equilibrium before it reaches chemical equilibrium. When this

happens, the element is lighter than the surrounding fluid because of its composition and, therefore, continues to rise.

It was also found that systems with a stable concentration gradient and an inverted thermal gradient are overstable if the overall density gradient decreases with height. In this case, an element displaced upward will return to the original position but will have lost heat in the process. Therefore, its density will be greater than the surrounding material and it will overshoot the equilibrium position.

These effects are quite important in understanding the role of gravity-driven convection and represent limitations on the control of Earth-based processes. They together with the morphological instability discussed in this report in the section on crystal growth may represent fundamental limitations on the control of Earth-based processes and establish a compelling motivation for low-g processing.

#### 5.1.6 Remaining Issues

1. There is a question of how well the basic studies of fairly simple systems outlined here relate to the more complex systems of interest to the industrial metallurgist. Can low-g studies be used to simplify such processes by separating out gravity effects? What are meaningful experiments to do?

2. Whether there is any potential advantage in preparing composite materials from the melt as compared to the use of conventional powder metallurgical techniques, such as liquid phase sintering and/or hot isostatic pressing, needs to be established.

3. Previous flight experiments with composite systems, both U.S. and German, have shown less-than-expected homogeneity in distributions of the second phase material. Some of the problems were brought about by failure to completely degas the starting powder, but other, more carefully done, experiments indicated that capillarity effects may be important in disrupting the distribution of the second phase. What governs these effects and how may they be controlled?

4. Possible density stratification effects in a single-phase, multicomponent liquid need to be evaluated to determine the importance of such effects. Are there important materials that are difficult to form in the compound phase because of stoichiometry problems? Can solidification in low-g solve such problems?

## 5.2 Directional Solidification

There are several current flight experiments and ground-based research tasks investigating directional solidification that might be enhanced by elimination of convective stirring and extremely high G/R processing.

### 5.2.1 Processing of Mn-Bi Magnets (Pirich)

Following the intriguing results obtained on the ASTP experiment in which Mn-Bi eutectic directionally solidified in space was observed to have a finer microstructure and enhanced magnetic properties, extensive ground-based and flight investigation has been initiated. This has resulted in several significant findings. The published phase diagram for Mn-Bi was found to be in error, and the composition used in the ASTP experiment was, in fact, hyper-eutectic. The space-processed sample had a finer microstructure than the control sample, in which composition varied because of convective stirring. The enhanced room temperature coercive strength was due to the heat treating that occurred in the gradient freeze solidification used in the ASTP furnace. It is known that heat treatment encourages the formation of a room temperature high coercivity phase, and control samples subsequently heat treated have shown similar performance.

The extremely high value for low-temperature coercivity shown by the ASTP samples appears to be unique and significant. The magnetic performance is surely related to the microstructure, but attempts to duplicate the magnetic performance of this sample by ground processing have so far been unsuccessful.

A eutectic sample processed on SPAR VI showed somewhat finer rod diameters compared to Earth-processed samples, and it also had finer spacing with more regularity. Magnetic data for this sample are not yet available.

### **5.2.2 Directional Solidification of Mn-Bi (Larson)**

This is an extension of the work described earlier by Pirich. The Solidification Experiment System (SES) being developed for the Shuttle will be used to obtain higher gradient and slower growth rates than can be achieved with the SPAR apparatus.

### **5.2.3 Directional Solidification of Metastable Peritectics (Larson)**

This is a ground-based effort to attempt to produce the metastable peritectic phase of  $\text{CoSm}_5$  by directional solidification. This research is a prelude to the extension of the previously discussed work with Mn-Bi to higher performance magnets, such as the Co/rare-earth systems.

### **5.2.4 Directional Solidification of Monotectic Alloys (Johnston)**

This effort is an attempt to produce fine dispersions of systems containing a liquid phase immiscibility gap by directional solidification. The effect of processing in stabilizing and destabilizing thermal configurations as well as in high magnetic fields is being investigated. Some success has been obtained by using Fe dopants in the Al-Pb system to break down the planar interface into a cellular interface. As the dense Pb phase nucleates and falls to the interface, it is trapped in the intercellular region and forms either fine rods or a series of fine droplets, depending on the composition, growth rate, and gradient.

### **5.2.5 Remaining Issues**

1. The role of gravity-driven convection in eutectic solidification may be more significant than previously believed. Additional experiments to establish this are required.

2. The processing of off-eutectic compositions in a convectionless environment offers the possibility of obtaining an additional degree of freedom in the composition of the sample; i.e., the relative amounts of alpha and beta phases can be selected at values other than the eutectic composition. This should be modeled analytically and confirmed experimentally. Possible applications should be explored.

3. The Bi/Mn-Bi system is extremely rich in magnetic properties, a fact that has led to much confusion in comparing magnetic properties of flight-processed samples with ground-processed samples. This whole issue needs to be clarified in light of what is presently known about the Bi/Mn-Bi system; e.g., can the microstructure of the ASTP sample (i.e., rod diameter) be duplicated or approximated by ground-based processing? How would the magnetic properties of such a sample compare with the ASTP sample?

4. The possibility of producing magnets with near theoretical coercive strength by improving the microstructure is intriguing, particularly if substantial improvements can be made in the intrinsic coercivity. However, an analogy between Bi-Mn/Bi and the peritectic systems such as Co-Sm is by no means obvious, and extrapolation from present results to the Co-Sm system is unwarranted. Only experiments can settle this issue.

5. High-gradient, high solidification-rate directional solidification might be used to process immiscibility gap alloys by minimizing the time from the nucleation of the immiscible phase until it is incorporated by the solidification front. This possibility needs to be explored.

6. The possible application of skin technology (the use of a thin oxide skin to retain the shape of an object in the absence of hydrostatic pressure) requires some careful consideration and a possible demonstration. Can this be approximated on the ground by some sort of liquid metal immersion technique?

### 5.3 Monotectic Alloys

The current programs investigating the formation and decomposition of monotectic alloys are described as follows:

#### 5.3.1 Solidification of Miscibility-Gap Alloys (Gelles)

Two SPAR flight experiments were conducted with Al-In. Massive separation was observed in the first experiment, but it was believed that insufficient time was allowed for homogenization. The experiment was repeated on SPAR V using a 16-hour soak above the consolute temperature. The same results were obtained, confirming,

in fact, that nongravitational forces are active in causing massive phase separations. The primary effort of this investigation is now being directed toward identifying and understanding these forces with the hope of ultimately being able to control them.

Various percentage compositions of Al-In were investigated on the SPAR flights. In all cases the In phase was found surrounding an Al core, which is consistent with the equilibrium configuration demanded by the minimization of the free energy. The mechanisms by which this configuration is achieved are not understood. Several possibilities exist: i.e., capillarity effects from one liquid phase wetting the wall, surface tension-driven convection at free interfaces, and migration of the minority phase droplets in the thermal gradient as a result of thermocapillary flows at their interface.

The SPAR results suggest that at least two of these mechanisms are important. Because In wets the graphite crucible better than Al, capillary wicking of the In to the container wall was most likely responsible for the separation of the Al-rich sample. This effect would not be important in the In-rich sample since the In is already in contact with the crucible walls; therefore, the interfacial energy cannot be lowered further by this mechanism. In this case it appears that the Al droplets may have been driven toward the center by thermocapillary flow. This was indicated by a series of droplets of varying sizes in the vicinity of the Al core. This effect should drive the In droplets to the center when they are the minority phase; however, this effect is apparently overwhelmed by the capillary effects at the container walls.

#### 5.3.2 Study of Immiscible Alloys in Spacelab (Gelles)

This is an extension of the work described previously using furnaces in the MEA and the SES to obtain more time and operating flexibility. The importance of surface tension convection will be assessed by using spring-loaded plungers in the crucible to eliminate free surfaces. Crucible wetting effects will be studied by choosing crucible materials with reverse wetting characteristics. Thermocapillary migration will be studied using directional solidification. Stability criteria will be studied by using systems with lower interfacial energy.



The results of this effort will be a better understanding of the formation of these unique alloys and their properties and a detailed knowledge of what is required to form various systems.

#### 5.3.3 Solidification of Al-In (Potard)

This is a complement to the Gelles SPAR experiment in that the graphite crucible is lined with SiC, which is preferentially wetted by Al. This will give an added data point to the establishment of the importance of the wettability of one of the phases with the crucible.

#### 5.3.4 Model Immiscible Systems (Lacy)

Because of the massive separation observed in previous experiments that attempted to form monotectic alloys, it became evident that experiments with transparent model materials were necessary in order to observe the separation process. Such experiments could establish the nature of any flows present and determine whether the separation was taking place in the two-phase liquid region or in the solidification process.

A number of model immiscible systems have been investigated. Two systems, diethylene glycol ethyl salicylate and cyclohexane/methanol, have been purified and characterized in terms of phase diagrams and surface activity. Measurement of droplet migration in thermal gradients has been initiated using small dimensional cells to suppress convective flows. Such measurements will also be conducted in KC-135 flights. Holographic techniques are being explored to give size distributions at different times in a volume large enough to avoid wall effects.

#### 5.3.5 Monotectic Alloys (Hellowell)

The objective of this study is to examine the monotectic reaction using directional solidification methods to obtain aligned composite structures. Of particular interest are the influence of gravity in the separation of the two liquid phases below a miscibility gap and their incorporation into the duplex growth front. Systems under investigation include Al-In, Cu-Pb, Cd-Ga, Al-In-Su, Cu-Pb-Al, Cd-Ga-Al, and transparent analogues such as  $(\text{CH}_2\text{CN})_2\text{-H}_2\text{O}$ .

### 5.3.6 Remaining Issues

1. There are alternative techniques for producing monotectic alloys; e.g., mechanical alloying, liquid phase sintering, hot isostatic pressing, rapid quenching, etc. There is reason to believe that monotectic alloys produced from the melt would have different properties because of the more intimate contact at the interface. This needs to be confirmed experimentally.

2. Succinonitrile-H<sub>2</sub>O is a nearly neutral buoyant transparent model system of a monotectic alloy. Experiments should be performed with this system to study the separation mechanisms involved.

3. Small samples of monotectic alloys can be rapidly quenched in a drop tower or ballistic aircraft flight. The early Ga-Bi experiments should be extended to other systems using these short-term, low-g capabilities.

### 5.4 Nucleation and Growth in Undercooled Melts

The current activities in this research area are:

#### 5.4.1 Preparation of Metallic Glasses (Lord)

The original thrust of this experiment was to investigate the formation of magnetic amorphous metals by deeply undercooling them in a containerless process. After an experiment on SPAR IV failed to melt, the objective was reassessed and it was determined that the cooling rate that was to be obtained in the SPAR electromagnetic (EM) levitator was probably insufficient to obtain the amorphous phase. Therefore, an easier metallic glass former (CuPdSi) was chosen, and the major emphasis was placed on measuring the viscosity of the system as a function of temperature and on studying the transition of the material when undercooled in quartz crucibles.

Recently some CuPdSi samples have been processed in free fall using the MSFC drop tube in an attempt to eliminate wall nucleation. Preliminary analysis indicates a glass structure was not obtained. It appears that the samples contained impurities that acted as nucleation sites and prevented deep undercooling. These tests were repeated with better sample material, and glass structure was confirmed by X-ray diffraction.

#### 5.4.2 Nucleation in Glass-Forming Alloys (Turnbull)

The main objectives of this research are: (1) to examine the factors that govern crystal nucleation in glass-growing alloy melts in order to determine which systems can form glasses and (2) to determine the conditions required to prevent nucleation before the glass transition temperature is reached. The systems  $\text{Au}_4\text{Si}$ ,  $\text{Pd}_4\text{Si}$ , and pure N have been studied by the droplet technique. The degree of undercooling possible with these systems varies widely with thermal treatments which alter the nature of the  $\text{SiO}_2$  surface film. Undercoolings as much as one-third of the liquidus temperature have been observed.

#### 5.4.3 Preparation of Metastable Phases by Containerless Processing (Lacy)

The A-15 compound,  $\text{Nb}_3\text{Ge}$ , has the highest known superconducting transition temperature ( $\sim 23$  K). This is a difficult compound to form because it is metastable and cannot be obtained by equilibrium processes such as normal solidification. Present techniques for forming  $\text{Nb}_3\text{Ge}$  are splat cooling and thin film co-deposition. The samples prepared by these techniques are quite thin. There is a desire to obtain bulk samples of such materials in order to relate superconductivity to lattice perfection. Such studies may hold the key to the development of higher transition temperature superconductors.

Pure Nb droplets have been undercooled in excess of 500 K in free fall using the MSFC drop tube. The droplets form single crystals with no shrink cavity in the interior. The outer surface is rough, indicating that the shrinkage associated with solidification was taken up by the interdendritic fluid.

$\text{Nb}_3\text{Ge}$  droplets have also been deeply undercooled and rapidly solidified in the drop tube. Unfortunately, accurate measurements of the amount of undercooling were not available at the time. An increase in transition temperature of  $\sim 2$  K was observed above the normal as-cast transition temperature (usually about 6 K), indicating that some of the A-15 structure may have been formed. New instrumentation has been added to the drop tube to obtain an accurate temperature history of the sample. The tests with the  $\text{Nb}_3\text{Ge}$  droplets will be repeated so that the

superconducting performance can be related to the amount of undercooling. A critical test will be to determine if the droplets formed in this manner can be brought up to the vicinity of 23 K transition temperature by annealing, which must be done for the material formed by the other techniques.

#### 5.4.4 Industrial Technical Information Exchange Program

The possibility of producing unique microstructure in samples by containerless processing in the EM levitator or by free-fall solidification in the drop tube has attracted some interest from industry. A process by which industrial or other users can submit samples for processing with no exchange of funds has been worked out with the MPS Commercialization Office. Samples have been processed for INCO under this program.

Most of the industrial interest lies in materials with melting points in the 1400° to 1600° C range, which are difficult to process in the drop tube under vacuum conditions because the radiation cooling is not efficient enough at these temperatures to remove the heat of solidification. Modifications to the facility will allow it to utilize gaseous He to provide additional convective cooling.

#### 5.4.5 Remaining Issues:

1. Concepts of what limits the undercooling process need to be reexamined. For example, how important are impurities in the sample as nucleation sites? Is it necessary to divide the sample into fine droplets in order to avoid such impurities? Is it possible to use various surface active coatings to deactivate such sites? Is homogeneous nucleation the ultimate limiting factor? How good are present theories of homogeneous nucleation?

2. One exciting prospect of deep undercooling experiments is the possibility of hypercooling; i.e., lowering the temperature in the liquid to the point where latent heat of solidification is less than that required to bring the material up to its normal melting point. In this case solidification is no longer controlled by the transport of the heat of fusion but can take place spontaneously, essentially freezing the atoms in place. This should produce an amorphous solid of any substance,

irrespective of its viscosity. How close can we approach hypercooling? For what systems is hypercooling theoretically possible (assuming the undercooling is limited by homogeneous nucleation)?

3. Relationships between the degree of undercooling, the solidification rate, and the resultant microstructure need to be developed. Especially important is the question of whether nonequilibrium phases can be produced in a controlled manner by such a process.

#### 6.0 Assessment and Recommendations

##### 6.1 Casting of Alloys and Composites

This aspect of the program has generated some industrial interest. An industrial guest investigator is being added to the Johnston experiment. Interest has been expressed by John Deere in studying the solidification of cast iron, and by INCO in investigating the solidification of some of the Ni-based superalloys used in turbine blades.

It has been found in dealing with members of the industrial community that they have little interest in participating in efforts that cannot yield results for several years. However, they are quite interested if tangible results can be obtained within 6 months to a year.

Very small castings can be solidified in the few seconds available in a drop tower. Somewhat larger castings can be solidified in the 20-40 sec available on KC-135 or F-104 aircraft. These are excellent activities with which to involve industry in the MPS program. Once they experience the methods for problem solving by using space, most will reexamine their research activities to see if there are other applicable problems (assuming they are treated properly by NASA).

Another area that is not well understood is the amount of density stratification in multicomponent systems in the liquid phase. It is generally believed that gravity-induced density stratification is negligible in solutions because the mass of individual atoms is so small that the geopotential contribution to the energy is overwhelmed by the energy associated with Brownian motion. While this is certainly true for true solutions in which the components do not interact, it may not be true for

certain metallic systems in which there is a tendency to form complexes. Experiments in centrifuges show that completely miscible binary systems, such as Pb-Sn, tend to be separated even in modest (5-g) fields. This might explain the difficulty in obtaining the compound phase of congruently melting systems, such as Al-Sb, in unit gravity.

## 6.2 Directional Solidification

It appears that one unique application for directional solidification in low-g may be the preparation of off-eutectic alloys. Since diffusion layers can be established in the absence of natural and thermosolutal convection, it should be possible to prepare regular rod or lamella structures provided by eutectic systems but in greatly expanded ranges of compositions. This should open new possibilities for controlling the microstructure of in situ composites.

Much has been said in the early literature about the increased gradient that can be obtained in low-g because of the lack of convection in the melt. Yet this has never been quantified. Calculation of the expected gradient in a convectionless melt is straightforward. What is not simple is the computation of the heat transfer in the ground-based systems with convective stirring.

Finally, more emphasis should be given to the preparation of systems that have liquid phase immiscibility gaps by directional solidification in low-g. This may be the only practical way to make such alloys that tend to decompose in nearly isothermal solidification. It may be possible to minimize the time the material spends in the miscibility gap by rapid solidification in a steep gradient. If this time can be made sufficiently short, the minority phase particles may become incorporated in the solid before they can grow large enough to migrate elsewhere.

## 6.3 Monotectic Alloys

A coherent systematic approach to the understanding of the decomposition of monotectic alloys even in low-g seems to be emerging. The recent addition of Professor Hellawell to this effort should aid this process. There are a number of experiments required to establish clearly

which mechanisms are important in this process. A considerable number of such experiments could be done by homogenizing the sample in unit-g and rapidly quenching it a few seconds in low-g. This can be accomplished in the drop tower or on ballistic aircraft flights. This method is much more efficient than space flights and can yield results in a much more timely manner. Such techniques should be used for screening samples and for rapid quenching experiments, leaving the slow-cooling experiments for later space flights.

A major key to understanding the behavior of monotectic alloys lies in the use of transparent model systems. Experiments of this nature can be performed on KC-135 flights and observed by ordinary photography. Such experiments are precursory to later Shuttle experiments using the FES to obtain growth rate data on the minority phase after it nucleates and begins to grow.

Additional emphasis is required in the alternative preparation of monotectic alloys such as powder metallurgy, splat cooling, etc., in order to form a basis of comparison for low-g processed samples that were solidified from the melt.

#### 6.4 Nucleation and Growth in Undercooled Melts

Lacy's pioneering effort using the MSFC drop tube drew considerable praise from a recent science review and has attracted attention from industry. The possibility of extending the undercooling experiments to larger samples and using slower cooling rates adds new dimensions to this work and should attract more experimenters. Leading experts, such as Professor Perepezko, have expressed interest in such experiments and should be encouraged to propose.

Results from the drop tube and from later flight experiments should be compared with EM-levitated samples. This will determine the effect of stirring on the nucleation and solidification of such systems. If, for example, it can be shown that there is little or no difference in the microstructure, ground-based EM levitation may offer a cheaper alternative to flight experiments.

A good theoretical model of an undercooled and/or hypercooled melt is badly needed. Such a model should predict the solidification front velocity, estimate the

the optical signature of the recalescence flash, and indicate something about the microstructure.

#### **6.5      Facilities Required**

The various flight furnaces presently available or under development (i.e., the SPAR ADSF, SPAR GPPF, SPAR and KC-135 casting furnaces, and the SES isothermal and directional solidification furnaces) will be able to accommodate most of the requirements for the foreseeable future, although a high-gradient furnace will be required eventually. The major requirement for furnace development at present is a small, rapidly quenched furnace capable of 1600°C for use in the drop tower or F-104 aircraft.

A special transparent, low-temperature furnace with rapid cooling capability will be required for KC-135 flights to observe the behavior of model immiscible systems. The FES with a special test cell would be ideal for use on the Spacelab experiments to study the behavior of model immiscible systems, particularly if the holographic system can give particle size information.

Containerless processing facilities such as the SPAR EM system or the single-axis levitator will be required for the containerless experiments. Automatic sample exchange is a virtual must. Eventually larger sizes will be required together with more sophisticated instrumentation.

#### **6.6      Supporting Research Required**

1. One of the critical problems in the study of the model immiscible systems is the ability to measure size distribution of a large number of particles. This has been demonstrated using in-line Gabor-type holography, but this technique requires that ~80 percent of the light traversing the test cell remain undeviated. This drastically limits the number density of particles that can be analyzed. Side-band holography can, in principle, be used with larger particle densities since the reference beam does not traverse the test cell. However, this has not been demonstrated nor have the limits been established.

2. An analysis of the heat transfer and gradient in a convectively stirred melt should be undertaken to compare with calculations of thermal profiles in



a convectionless melt. Such an analysis should consider diameter, aspect ratio, material properties, and method of heating.

3. The effect of geopotential on density stratification of various metallic or model systems should be investigated. Such an experiment could consist of a long isothermal column containing a multicomponent, single-phase melt. At various times samples could be taken at different heights and analyzed for composition.

4. Better documentation is needed to sell the program to potential industrial users. One very useful medium is computer-generated movies comparing various unit-g solidification processes with the same process in low-g.

## **FLUIDS AND CHEMICAL PROCESSES**

## Fluids and Chemical Processes

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## Fluids and Chemical Processes

### 1.0 Introduction

Although the gravitational contribution to the chemical potential is usually negligibly small, many processes are controlled by mass and heat transport which are affected by gravity-driven convection or sedimentation. Often this occurs in complicated ways in which gravity-driven flows are coupled with nongravitational flows such as surface tension-driven convection. Experiments in low-g can simplify such problems by eliminating one set of flows so that the nongravity components may be isolated and studied with a degree of freedom not otherwise possible.

In some processes it is desirable to keep a system of two or more components in suspension in order to study nucleation and growth or ripening of one of the phases. By eliminating all but diffusion transport, many complicated systems can be made tractable. By eliminating the hydrostatic pressure, free and interfacial surfaces are controlled only by surface tension. This greatly simplifies the study of wetting and spreading and the measurement of contact angles, especially in systems near critical phase transitions where interfacial tension approaches zero. Also, the usually insignificant gravitational contribution to chemical potential is not negligible near a critical phase transition since the other terms go to zero. Therefore, there may be some advantage in studying critical point phenomena in a low-g environment.

### 2.0 Objectives

The objectives of the fluids and chemical processes program are to explore the role of gravity in various fluid and chemical processes, determine where low-gravity experimentation may provide extension of research capability, and involve the scientific community in developing meaningful space experiments.

### 3.0 Justification

There appears to be a substantial interest among researchers in the field of fluids and chemical processes in utilizing space experiments as a tool to extend their research effort, as was evident from the response to a

Fluids and Chemistry Workshop hosted by The University of Alabama in Huntsville (UAH). Most of the potential experiments discussed by the attendees were oriented toward scientific research, although there were several experiments that may have industrial applications

In addition to these potential experiments, there are a number of experiments involving fluids and chemical processes that support other materials processing disciplines by providing basic information on the limitation imposed by a unit-g field, the nature of nongravity-driven flows, and the behavior of the flows resulting from the low-level, nonsteady residual accelerations associated with the spacecraft environment. These effects must be understood in order to design and carry out the other experiments in a meaningful manner.

#### 4.0 Background

##### 4.1 Fluid Effects from Spacecraft Motion

It is well recognized that gravity-like accelerations do not vanish in an orbiting spacecraft but are reduced to a very low level; i.e.,  $10^{-4}$  to  $10^{-6}$  g. The residual accelerations stem from atmospheric drag, various inertial effects arising from the spacecraft motion about its center of mass, Keplerian effects arising from the fact that every free object in the spacecraft is in a slightly different Keplerian orbit, impulses from attitude control thruster firings, and g-jitter from crew activity or other mechanical vibrations. It is important to know the levels of acceleration to expect from these effects and the effects of such accelerations on the motion of fluids and gases in containers.

A common misconception is that the flows produced by a micro-g acceleration background on an orbiting spacecraft are equivalent to those produced by unit gravity in a container in which the dimensions are reduced by a factor of 100. This argument is based on the fact that the Grashof number, which characterizes buoyancy-driven convection, is proportional to  $g l^3$ . It would be true if the accelerations were steady and unidirectional. Such is not the case, however.

In a manned spacecraft, the motion of the crew produces the largest accelerations, usually on the order of  $10^{-3}$  to  $10^{-4}$  g. Such motion produces no net

momentum to the spacecraft and, therefore, may be modeled by two equal and opposite impulses separated by a short time interval. If the fluid has a density gradient normal to the acceleration, the first impulse will impart a slight convective velocity to the fluid that will be nullified a short time later by the second impulse. If the time between impulses is small compared to the dimension of the container divided by the velocity imparted to the fluid, the net displacement of fluid will be small. There may be some residual fluid motion because the fluid system is not conservative, but these are second-order effects. Generally, the higher frequency jitter would be expected to produce less fluid motion than the lower frequency terms because the fluid will move less between the compensating impulses.

Thruster firings from the Shuttle VCS system can be expected to occur more or less randomly through the mission to maintain attitude control. Unlike the Apollo Command Service Module (CSM), on which the thrusters fired as a couple, the Shuttle utilizes only one set of thrusters for attitude control. This means that each thruster firing will impart an uncompensated linear acceleration on the order of  $10^{-4}$  g in addition to the attitude control torque. This will initiate a small fluid flow in a system containing transverse density gradient. Since the VCS firings are of very short duration (40 msec pulses), the total impulse is very small. However, since there is no compensating impulse in the opposite direction, the flow initiated by the impulse will continue until it is damped out by viscous forces.

The aerodynamic and Keplerian forces are of lower level but are more or less constant in magnitude. They will, however, vary in direction depending on the spacecraft orientation. Because these forces have very low frequency (on the order of the spacecraft orbital period), they may be the dominant factors in producing flows. It may be possible to minimize the disturbances by changing the spacecraft orientation to cause these forces to time average out over a short enough period to minimize the flow disturbances. The behavior of compressible fluids such as gases may be quite different from the behavior of virtually incompressible fluids in a low-g environment. Any difference in motion between the container wall and the fluid must be transmitted by a pressure disturbance that propagates through the media. Substantially more flow will take place in a gas than in a liquid that completely fills its container. This may account for the

departure from diffusion-controlled transport observed in the chemical vapor experiments conducted on Skylab and ASTP by Wiedemeier.

#### 4.2 Surface Tension-Driven Convection

One of the major driving forces for convective flow in the absence of gravity is surface or interfacial tension, often referred to as Marangoni flow. Because such convection can produce significant flow effects in space experiments as well as in Earth-based experiments, there is considerable interest in understanding this phenomenon.

Like buoyancy-driven convection, there are two distinct types of flows that can result from surface tension-driven convection. An instability exists when a fluid with a free surface is heated from below the surface. Since surface tension for most materials decreases with temperature, the system could lower its interfacial energy by exchanging its warmer subsurface fluid with the surface. As in unstable buoyancy-driven convection, flow in the form of Benard cells occurs only after a critical Marangoni number is exceeded. This has been demonstrated in a space experiment and can also be observed on the ground by using a sufficiently thin layer of fluid in order to stay below the critical Rayleigh number that would result in the complicating effect of buoyancy-driven convection.

Of more interest is the surface tension flow that results whenever there exists a gradient of surface tension along a surface. Such a gradient can be caused by either thermal or compositional variations. In this case, as in the corresponding natural convection resulting from a density gradient perpendicular to the gravitational force, flow begins immediately, without the necessity of exceeding a critical Rayleigh or Marangoni number. This type of flow is more difficult to study in the Earth's gravity field because virtually every situation involving a gradient in surface or interfacial tension is also accompanied by gravity-driven flows. It has been shown in drop tower tests that surface tension-driven flows are not confined to the surface layer but can also produce mixing at considerable depths.

Such flows are expected to play an important role in a number of processes considered for low-g application as well as in some Earth applications. For example, the

thermal migration of bubbles or immiscible droplets is driven by temperature variation in surface or interfacial tension. These may be important techniques for fining glass or coalescing immiscible phases in phase partitioning. On the other hand, this could also be an unwanted mechanism that causes phase separation in the preparation of monotectic alloys. It is also suspected that Marangoni flows play an important role in flame propagation on the surfaces of flammable liquids. The lower surface tension near the flame causes fluid to "pull away" from the flame, resulting in a slight depression. The return flow feeds fresh fluid from beneath the surface into the flame.

Perhaps the most compelling reason for studying Marangoni convection is its importance in floating zone crystal growth. This process involves free surfaces and large axial temperature gradients. The convective transport in a unit gravity field is obviously very complicated because it involves natural as well as unstable buoyancy-driven convection coupled with surface tension-driven convection. Performing such experiments in a low-g environment provides a method for simplifying the flows by eliminating the buoyancy-driven effect, thus isolating the surface tension effects so that they can be studied individually.

One of the most important aspects in the study of surface tension-driven convection is the effect of small surface active impurities. Accurate measurement of surface tension has always been a difficult problem because of the difficulty in obtaining and maintaining sufficient purity of the sample. Even the slightest trace of a surface active component will arrange itself on the surface in such a way as to alter and usually reduce the surface tension gradient, thereby reducing the flow. In fact, several space experiments involving free surfaces did not show evidence of Marangoni flow. Although the experiments are by no means definitive, they do indicate that control or even elimination of such flows may be possible by the addition of selected surface active components.

Generally, Marangoni flow must be considered in systems that have either liquid-liquid or liquid-vapor interfaces. The no-slip boundary condition that applies to liquid-solid interfaces does not allow surface tension-driven flow. However, it is not known what happens in a system in which the liquid does not wet the wall. In one-g the hydrostatic pressure forces out any vapor between



the liquid-solid interface, but the type of interface that exists between a nonwetting liquid and a solid in low-g is not clearly understood.

Although an experiment was flown on ASTP to investigate this question, there was no conclusive evidence for Marangoni flow. Other nongravitational flows such as volume change effects during solidification or segregation effects could have affected the observed results. Therefore, the question is still unsettled.

#### 4.3 Critical and Interfacial Phenomena

One of the recommendations in the report of the Committee on Scientific and Technological Aspects of Materials Processing in Space (STAMPS) was that investigation of critical phenomena may be a worthwhile scientific endeavor. Near phase transitions the correlation length becomes long. Since the difference between the chemical potentials of the two phases vanishes at the critical point, the small contribution from the difference in gravitational potential over the correlation length may become significant. Also, since the density of the two phases is virtually always different, gravitational sedimentation will cause rapid phase separation as the second phase droplets nucleate and start to grow. This limits the time and size range over which the transition can be observed.

As systems that have two immiscible liquid phases approach the transition to a single liquid phase, the interfacial tension as well as the contact angle goes to zero. The prevalent theory, developed by Cahn, predicts that one of the phases becomes perfectly wetting at the critical point. This is difficult to observe in the laboratory because the radius of the meniscus between the two phases becomes vanishingly small as the hydrostatic pressure becomes much greater than the interfacial tension. The existence of one phase that becomes perfectly wetting may be the key to the rapid phase separation observed when attempting to form monotectic alloys.

Several cases of apparent anomalous wetting behavior were observed in Skylab and ASTP experiments that have not been resolved. Generally it was found that systems that were believed to wet one another apparently did not in the space environment. Because the results were unanticipated there were generally not adequate controls to establish definitively whether the anomalous wetting was

caused by contaminants or whether the lack of hydrostatic pressure somehow alters the wetting behavior; e.g., by allowing a vapor film to form between the liquid and the container.

Another interesting effect that was observed in several previous flight experiments was an apparent curvature in concentration profiles of diffusion-controlled transport, suggesting some sort of interaction of the solute with the walls. If this effect is real, it could strongly influence diffusion measurements made on the Earth since such measurements rely on capillary tubes to suppress convection. Wall effects, if present, could easily confuse such measurements because of the large surface-to-volume ratio.

#### 4.4 Crystal Growth

Fluid and chemical phenomena relate directly to crystal growth since they provide transport of heat and material to the growth interface; in some growth techniques, growth occurs as a result of the release of a component by a chemical reaction. The use of transparent growth systems affords an opportunity to study the growth environment in great detail by use of optical techniques and to relate observed growth phenomena to this environment. From such studies we have begun to learn a great deal about the control of the growth process.

In addition to the study of growth phenomena, there are a number of complex organic systems that are difficult to crystallize but whose structure and properties are of great interest to biologists and chemists. Techniques exist to grow some of these systems to produce samples of sufficient quality for X-ray diffraction analysis, which has produced a wealth of data on the structure of macromolecules such as immunoglobulins, catalase, concanavalin A, hexokinase, etc., as well as linear chains of transition metal complexes of  $\alpha$ -amino acids. There are, however, limitations associated with the use of X-ray diffraction that can be overcome by using neutron diffraction. For example, information concerning the location of hydrogen atoms is difficult to obtain from X-ray diffraction because the X-ray scattering factor is proportional to the number of electrons surrounding the nucleus. Neutrons respond readily to hydrogen atoms. Also, they are non-ionizing and, therefore, produce less damage in the crystal, and they allow the spin of the atoms in the structure to be determined.

Good X-ray diffraction data can be obtained from crystals as small as 0.3 mm in all directions, whereas neutron diffraction would require a crystal in excess of 3 mm in all dimensions. Present growth techniques have been largely unsatisfactory for producing macromolecular crystals of these sizes.

If the diffusion-controlled environment and quiescent conditions in space can be used to advantage for the growth of such crystals, this could be a significant contribution to biomedical science.

#### 4.5 Industrial Processes

There are a variety of processes important to industrial applications that may be studied in a low-g environment for the purpose of understanding the role of gravity effects or for taking advantage of the virtual lack of buoyancy-driven convection, sedimentation, or hydrostatic pressure in order to achieve better process control. For example, seeded polymerization of latex may be used to grow monodispersed spheres in a size range that is virtually inaccessible to ground-based techniques because of creaming or sedimentation effects. Such spheres would be useful as standards for calibrating counters, sizing membranes, and possibly other biomedical applications. There may even be some commercial advantage in making such a product in space.

The absence of sedimentation provides an opportunity to study the role of chemical fining of glasses by eliminating the competitive process of Stokes bubble rise. Chemical fining agents certainly will become more important in the future as energy costs continue to rise. Because glass is viscous, Stokes velocities of bubbles are extremely low, and very long high-temperature soaks are required. Chemical agents are known that help reduce the time, but the mechanism is not well understood. The difficulty of containing a bubble in a small container for study may be appreciated.

Another endeavor that takes advantage of the absence of sedimentation is the study of Ostwald ripening. This is a process by which a nearly monodispersed second phase evolves into a distribution of sizes with the larger particles growing at the expense of smaller particles in order to minimize the interfacial energy of the system. This effect is quite important in a number of metallurgical applications in which the size of a precipitated

second phase is altered by heat treating. Although the phenomenon of Ostwald ripening has been known for a number of years, there is still no satisfactory agreement between theory and experiment because of the difficulty of maintaining stable suspensions of the precipitating phase long enough to obtain good size distributions.

Electrochemical deposition is a process that must be influenced considerably by gravity because of Joule heating of the bath as well as solutal convection from concentration gradients. Yet the literature reveals that very little work has been done to understand the role of gravity-driven flows. In some cases it is desirable to incorporate inert particles of a second phase into an electroformed product to improve its properties. Maintaining such particles in a suspension and incorporating them uniformly into the structure is difficult in the laboratory.

Another application that may have industrial interest is the opportunity to study agglomeration and flocculation of suspended sols. These processes are important in many industrial waste disposal and purification operations. There are competing theories describing the mechanisms involved in these processes that are difficult to test because sedimentation interferes with the measurements.

## 5.0 Experiment Status and Remaining Issues

A cadre of experimenters who can benefit from the use of low-g research has been identified from a workshop held in July 1979. From this group of investigators will come proposals to study gravitational effects on critical point phenomena, Ostwald ripening, transport phenomena, crystal growth, and various separation processes.

Current activities in the various specific categories are described in the following sections.

### 5.1 Fluid Effects from Spacecraft Motion

There are presently no approved flight experiments to observe and measure vehicular-induced flows.

Dr. Dressler, NASA Headquarters, is developing analytical models to describe the response of a contained fluid with a thermal gradient to transient low-level

accelerations. This work is being supported by a computer analysis at Lockheed, Huntsville.

#### 5.1.1 Remaining Issues

1. The results of Dressler's work predicting the effects of spacecraft motion on fluid flow should be compared with the earlier work of Ostrach to determine if there are significant differences. A critical experiment should be designed to detect such differences if they are significant.

2. The effects of long-period, low-level forces arising from aerodynamic drag and Keplerian forces should be carefully analyzed. The optimum vehicle orientation for minimizing such effects should be established.

3. Dressler's work should be extended to determine the importance of the vorticity produced by the effects of space rotations. The magnitude of these effects on fluids in filled containers should be compared to centrifugal effects associated with the rotation.

4. The effects of spacecraft motion on compressible fluids (i.e., gases) should be considered. In particular, it should be determined if such effects could have been responsible for the anomalous effects in mass transfer observed by Wiedemeier on Skylab and ASTP.

5. A straightforward, well-written users handbook describing fluid behavior under transient and low-g accelerations expected in Shuttle is badly needed to allow investigators to assess their experiments and to determine the g-levels that can be tolerated.

6. Some form of flow visualization experiment should be carried out on one of the early Shuttle flights. Although such a flow could in principle be calculated given the acceleration profiles, it may be simpler to actually fly an experiment. Also, the combined flows and stilling times from all of the low-level effects would be more meaningful to a prospective user if he could actually see them.

#### 5.2 Surface Tension-Driven Convection

An active working group under the leadership of Dr. Fowle, A. D. Little Corporation, is developing the

concepts for an Analytical Float Zone Facility. The effort involves several research activities that are dedicated to the study of surface tension-driven convection. These are discussed in the chapter on Crystal Growth, Section 5.4.

Studies of the migration of bubbles and fluid droplets are discussed under Section 5.3.4 of the chapter on Solidification of Metals, Alloys, and Composites and in Section 5.5.3 of this chapter.

#### 5.2.1 Analysis of the Float Zone Process (Brown)

This research effort involves a computational simulation of the fluid and heat transfer that takes place in a float zone crystal growth process. Analytical models are being developed for the melt-solid interface to examine the effects of both natural convection and Marangoni convection. Such models are essential for determining the conditions that must be controlled in order to obtain flat interfaces in either ground-based or space-flight float zone crystal growth.

#### 5.2.2 Thermocapillary Flows and Their Stability: Effects of Surface Layers and Contamination (Davis)

This research effort consists of a theoretical analysis of the fluid mechanics and heat transfer of motions driven by surface tension gradients. The geometries will include thin films, deep films, and floating zones. In particular, the effects of contaminants, such as a third-phase film on the melt-gas interface or surface tension-driven flows, will be considered. Also, the stabilities of flows with and without contaminating surface films will be investigated.

#### 5.2.3 Remaining Issues

1. The effects of possible surface active contaminants on surface tension-driven flows must be evaluated. Particular attention should be given to the contaminants usually present in candidate materials for float zone crystal growth and to possible contaminants or films that could be added to suppress unwanted flows.

2. The extent to which such flow can be studied on the ground must be established.

3. The nature of the interface between a fluid and a non-wetting container needs to be clarified. In particular, it must be determined if surface tension convection can occur at such an interface.

### 5.3 Critical and Interfacial Phenomena

There are presently no approved flight experiments or ground-based efforts to develop flight experiments to utilize the low-g environment to study critical or interfacial phenomena.

#### 5.3.1. Remaining Issues

1. The importance of the variation in geopotential contribution to the free energy over the correlation length in a critical phase transition should be assessed and a determination made whether the elimination of this effect would be sufficient justification for a space experiment.

2. What can be learned by studying the nucleation and growth associated with a critical phase transition using a low-g environment to keep the second phase in suspension should be assessed and a determination made whether such a study would be sufficient justification for a space experiment.

3. A study should be made to determine whether there are sufficient reasons to eliminate the distortion of the interface from hydrostatic pressure to justify going to space in order to study wetting and spreading phenomena in the degenerate case near a critical phase transition.

4. The cause for the anomalous wetting phenomenon observed in several Skylab and ASTP experiments is still not identified. Neither has it been determined if this phenomenon is of sufficient scientific interest to merit a systematic investigation.

5. The cause of the curved interfaces observed in several previous space experiments involving diffusion is not yet understood. It would be of interest to know whether this resulted from interactions between the solute and the wall, and if such effects are important in Earth-based diffusion measurements performed in capillaries.

#### 5.4 Crystal Growth

Current efforts to investigate the fluid and chemical aspects of the growth environment are:

##### 5.4.1 Growth of TGS in Low-g (Lal)

See Section 5.2.1 in the chapter on Crystal Growth.

##### 5.4.2 Growth of Crystals in the Space Environment (Shlichta)

The purpose of this experiment was to investigate the growth of crystals in the space environment by characterizing the growth environment and how it changes in response to vehicular disturbances and to relate this environment to growth effects in the crystal. It was planned to measure thermal and concentration profiles simultaneously in the growth solution using interferometry and absorption measurements. Unfortunately, a suitable system was not determined in time to make design inputs to the Fluids Experiment System; hence, the experiment is still in the definition stage.

##### 5.4.3 Growth of Alloy-Type Semiconductors (Wiedemeier)

See Section 5.4.1 in chapter on Crystal Growth.

##### 5.4.4 Transport Phenomena in Vapor Crystal Growth (Rosenberger)

See Section 5.3.3 in chapter on Crystal Growth.

There is no current NASA-sponsored research directed toward the growth of macromolecular crystals.

##### 5.4.5 Thermosolutal Convection (Coriell)

See Section 5.1.5 in chapter on Solidification of Metals, Alloys, and Composites.

##### 5.4.6 Remaining Issues

1. A critical space experiment is required to resolve the anomalous growth observed by Wiedemeier in Skylab and ASTP. Ways of reconciling this question in the laboratory should also be explored. In particular, the



possibility of motion of the growing crystals in the tube must be considered together with possible flows in the vapor from vehicular motions.

2. Efforts should be initiated to investigate the limiting factors in growth of macromolecules in one-g to determine whether the low-g environment can be used effectively in this important research.

### 5.5 Study of Industrial Fluid Chemical Processes

There are presently several approved flight experiments aimed at the study of fluid chemical processes of interest to industry. These are:

#### 5.5.1 Monodispersed Latex Spheres (Vanderhoff)

This effort will explore the possibility of performing seeded polymerization in low-g to avoid the problems of creaming and sedimentation as the particles grow and change density. If successful, this could provide a method for routinely producing monodispersed spheres in a size range that is difficult to obtain by other techniques.

Ground-based experiments are continuing to obtain kinetic data and to evaluate alternative methods for growing such spheres. Flight hardware has been defined, and negotiations are underway to produce reactors to fly on early Shuttle flights.

#### 5.5.2 Glass Fining in Space (Weinberg)

The objective of this experiment is to study the effectiveness of chemical fining agents. By elimination of buoyancy, preformed bubbles in a glass melt will remain suspended so that the dissolution of the bubbles may be observed over a long period of time.

#### 5.5.3 Motion of Bubbles under Thermal Gradients (Wilcox)

This experiment investigates the fining of glasses by the application of a thermal gradient that causes the bubble to migrate because of thermocapillarity flows. Although the theory of bubble motion in a thermal gradient has been worked out and demonstrated in some systems, there are many uncertainties, such as the dependence of

surface tension on temperature and the role of possible surface active contaminants. Because of the potential importance of this process in the fining of glasses produced in space, an experiment is required to answer some of these questions.

An experimental apparatus is nearing completion and will be flown on a SPAR flight in the near future.

#### 5.5.4 Electroplating in Low-g (Askins)

An electroplating experiment is being developed by Ms. Askins (MSFC), Dr. Riley (UAH), and Dr. Fisher (INCO) under a Technical Exchange Agreement. The objective is to observe the fluid flows associated with electroplating both in unit-g as well as in low-g in order to assess what effects might be expected to occur in electroplating or electroforming. Particular attention will be given to the incorporation of inert particles into the electroform.

Cells have been built and are ready for flow measurements in the laboratory. These cells have also been flown on KC-135 aircraft for low-g flow visualization and eventually will be flown on Shuttle as part of the Minimal Interface Shuttle Experiment (MISE).

#### 5.5.5 Remaining Issues

1. The amount of stirring required in the preparation of monodispersed seed latex in low-g to provide good mixing and heat transfer must be determined together with the size particles that can be held in suspension by this stirring in one-g. It must be established whether or not the same goal can be accomplished on the ground by using rotational methods to keep the particles suspended without exceeding the critical stirring that produces agglomeration.

2. New concepts of how low-gravity research might benefit various industrial processes by being able to isolate certain aspects for detailed study must be explored. Examples are how a better understanding of thermosol-utal convection, Ostwald ripening, and dendritic growth might be applied to the metals-forming industry, or whether a low-g experiment could contribute to the understanding of flocculation and agglomeration, which might be of use to industrial purification processes.

## 6.0 Assessment and Recommendations

### 6.1 Fluid Effects from Spacecraft Motion

Most of the experimenters in the MPS program do not have extensive fluid mechanics backgrounds. In many cases they are unable to assess the magnitude of the gravity effects on Earth from which they are trying to escape by going to space. They certainly are in no better position to evaluate their requirements for acceleration levels in planning their space experiments.

Also, a number of misconceptions about the nature of the g-levels encountered in a spacecraft and their effects appear to exist among some experimenters who do not differentiate between the low-level, quasisteady forces from drag and the short-duration, impulsive, higher amplitude forces that occur more or less randomly. This lack of understanding is reflected in the specification of g-levels in the experiment requirements documentation. Obviously, the experimenter would like no accelerations. Knowing this is not possible, he specifies " $10^{-4}$  g" and hopes for the best. What is really needed is a critical assessment of the fluid flow that can be tolerated in the experiment. This can then realistically be translated into an allowable g-level spectrum, or perhaps a more meaningful specification would be integrated impulse as a function of integration time. This would be a measure of fluid displacement.

These misconceptions are beginning to be cleared up thanks to the earlier work of Ostrach and the more recent work of Dressler. However, neither researcher's work is in a form that is readily useful to a typical investigator. What is needed is an experimenter's handbook showing him how to evaluate the gravitational effect in his experiment both on the ground and in a low-g environment.

A critical assessment is needed of the various papers dealing with the effects of the types of low-g accelerations expected in an actual flight. This assessment is required to develop the experimenters handbook, mentioned previously, but it would also serve to identify remaining problems that have not been properly addressed and to determine if critical experiments are required to evaluate the various theories. Of particular importance

is the question of the behavior of compressible fluid, such as gases, in a low-g environment. Gebhart's original paper on this subject has not gained much acceptance but does point out that significant effects can be expected from random, low-level accelerations in a vapor transport process. This should be reexamined in the light of Wiedemeier's result.

An additional study that should be undertaken along this line would address the question of the optimum orientation of the Shuttle to minimize accelerations at the experiment. It has been tacitly assumed that a z-local vertical, gravity gradient stabilized motion would provide the best possible low-g environment, but this is by no means obvious. For example, this configuration produces a continuous drag acceleration that always acts in the same direction, whereas in an inertial orientation, the drag acceleration would time-average to zero over an orbital period. This could be one of the most important factors in the behavior of fluids in low-g.

Finally, some form of flow visualization experiment should be done on one of the early missions. Despite the objections of some members of the fluids community that such an experiment is trivial because such flows can be calculated, the problem is complicated by many different factors, all of which are not known. There are assumptions that have to be made in order to make the analysis tractable, there may be unsuspected coupling between various effects, and the graphic detail of the flow patterns would help experimenters visualize what happens. Such an experiment need not be complicated. A small test cell containing marker particles could be photographed with a 16 mm camera over a period of time. A thermal gradient could be imposed by thermoelectric devices, as is done on SPAR experiments. Various spacecraft maneuvers could be scheduled during the run to assess the effects.

## 6.2 Surface Tension-Driven Convection

The topic of surface tension-driven convection as it pertains to float zone crystal growth has been adequately covered in Section 5.4 of the chapter on Crystal Growth. There are some additional problems, however, that should be considered in the fluids and chemical processes program.

The question of surface tension-driven convection in containers with nonwetting walls should be settled once

and for all since it has been involved in previous experiments to explain unanticipated effects and will probably be involved in the future. The question to be addressed is what is the nature of the interface between a poorly wetting liquid and a solid in the absence of hydrostatic pressure? A thin layer of vapor between the liquid and solid is not inconceivable and would surely allow free motion at the interface. The question could be settled rather easily by observing the motions of liquids in partially filled containers that have either a thermal or concentration gradient imposed. Such an experiment could be performed in the MISE. If a more sophisticated effort is required, the FES would be an ideal experiment facility.

Another effect involving surface tension-driven convection that should be investigated more fully is the migration of bubbles and immiscible liquids in a thermal gradient. The classical theory of this effect (Young, Block, and Goldstein) assumed that the bubbles remain spherical despite the influence of surface tension gradients. This, of course, does not happen; the bubbles will deform in a way to lessen the unbalanced forces. Subsequent treatments of this problem argue that the deformation is a small perturbation to the solution. Some experimental confirmation has been obtained, but the difficulty of doing such experiments in a gravity field is great. A well-controlled experiment in low gravity with a large enough bubble to allow measurement of the reformation would be most welcome since several of the experiments on glass fining, glass shell production, and monotectic alloys depend on this effect.

### 6.3 Critical and Interfacial Phenomena

No critical point experiments are currently being sponsored by the MPS program, although three such experiments are currently part of the Physics and Chemistry Experiments in Space (PACE) program. Several meetings have been held with leading researchers in the field (Cahn, Moldover, Goldberg, and Sanger) to explore possible experiments that could utilize MPS facilities.

With some modifications, the laser in the FES could be useful in detecting critical opalescence and nucleation events by analyzing the scattered light. (A linear array could possibly be installed in the test cell

to accomplish this.) The utilization of holography to measure size distributions of the condensed particles appears to be very useful, provided this can be demonstrated. The application of the shadowgraph capability of the FES holograms would be very useful for precisely determining the interface shapes in critical wetting experiments.

Practically all of the critical point experiments require milli-Kelvin or better temperature control. This is beyond the present FES capability but could be incorporated into a special test cell.

Very little effort has been expended in evaluating the anomalous wetting behavior or the peculiar diffusion fronts observed in some of the Skylab and ASTP experiments. Since these results were unanticipated, the lack of experiment control makes it difficult to say very much about what might have happened. Some exploratory experiments should be tried on the MISE to establish whether these effects are worth investigating further.

#### 6.4 Crystal Growth

The discussion of crystal growth is adequately covered in Section 6.0 of the chapter on Crystal Growth. Additional details on the growth of macromolecular crystals are given in Section 6.5 of the chapter on Bioprocessing. Similar requirements for the growth of long chain macromolecular structures have been identified from chemists. These long amino acid chains, such as hippurates, can form linear structures for bonding Fe, Co, or Ni and exhibit unique one- or two-dimensional magnetic properties. Similar chains (such as TTF-TCNQ) exhibit remarkable linear conductivity, rivaling metallic conductors at low temperatures. Such systems have caused some researchers to speculate on the possibility of room-temperature organic superconductors. If it can be shown that the low-g environment can be used to enhance the growth of such systems, there would be a major scientific payoff.

#### 6.5 Study of Industrial Fluid Chemical Processes

The efforts described are a good start in involving researchers to consider space as a problem-solving capability. In addition to the efforts described, a proposal is in preparation (Kuczynski, Notre Dame) to study Ostwald

ripening in order to distinguish between the classical theory of Lifshitz, Slyozov, and Wagner (LSW), and the proposed Kuczynski theory. This need arises because the classical (LSW) theory does not correctly explain the observed distributions in thorium dispersion strengthened Ni/Cr alloy used in jet engines. Kuczynski and his coworkers have spent years attempting to obtain an experimental test of his theory, only to be frustrated by convection and sedimentation. Space appears to offer a method to resolve this dilemma.

Other potential experiments were identified by the Fluids and Chemical Workshop and may result in proposals to the next Announcement of Opportunity (AO).

#### 6.6 Facilities Development

The FES is considered to be the primary facility for the fluids and chemical processes experiments. The holographic optics provide a versatile capability for thermal and/or compositional profiling. This capability could be enhanced by use of localized fringe analysis to permit a truly three-dimensional index of refraction analysis rather than the total integrated path analysis provided for in the present design. This would entail the addition of a diffuser plate in front of the test cell.

Many of the proposed applications of the FES hinge on the ability to obtain particle size distributions with a large number density. While this is possible in principle, this capability needs to be explored and demonstrated. Limiting resolution and maximum number density need to be established.

Unfortunately, the one thing holography does not do well is detect moving particles. Flow visualization experiments using marker particles require a camera with a chopped shutter. No provision exists in the present FES for locating a simple camera. This could probably be best accomplished by the construction of a simpler system consisting of test cell, lights, and camera.

A concept to provide such experimental capability is being studied in the Science and Engineering Directorate, MSFC. The objective is to beat the high cost of experiment development and integration by designing a MISE package to fit into available lockers on the mid-flight

deck. Such a package could accommodate several of the experiments described in this document.

In addition to flight experiments, several ground-based facilities are required to investigate low-g fluid and chemical experiments. A Plateau tank (neutral buoyancy) has been constructed to investigate coalescence and interfacial phenomena as well as to demonstrate the classical low-g experimental techniques. Also, a rotational suspension system has been constructed to investigate possible techniques for keeping materials of different densities in suspension.

#### 6.7 Required Research Activities

It is incumbent on the fluids and chemical processes program to provide fluid dynamics support for the other elements of the program. One of the major shortcomings of the MPS program is that many of the processes that occur in one-g are not really understood.

For example, in order to set an operational limit on the capability of a continuous flow electrophoretic chamber, it is necessary to know the magnitude of convective disturbances or stability limit for a flowing system subjected to horizontal as well as vertical thermal gradients. Stability analyses have only been done for static systems with vertical thermal gradients.

Similar problems exist in attempting to estimate the convective flows and thermal transport in a crystal growth experiment without a flowing system but with radial thermal gradients driving flows that are stabilized by thermal or composition gradients. Such problems simply have not been analyzed by fluid dynamicists.



**CONTAINERLESS PROCESSING, GLASSES,  
AND REFRACTORIES**

## Containerless Processing, Glasses, and Refractories

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## Containerless Processing, Glasses and Refractories

### 1.0 Introduction

The MPS program has kindled new interest in containerless processing; i.e., the ability to melt, solidify, or otherwise process a sample without physical contact. There are a number of reasons for wanting to process material without containers in space: the ability to measure physical properties of refractory or highly corrosive materials; the ability to produce ultrapure specimens of various materials; the formation of unique glasses from materials that are reluctant glass formers, either because of their corrosive nature or their tendency to devitrify because of container wall nucleation; the ability to study homogeneous nucleation and the associated time-temperature-transition (T-T-T) relations in an unambiguous manner; the ability to study the solidification of deeply supercooled materials; and the ability to fabricate unique shapes and configurations without sagging or physical contact, such as highly concentric glass shells for initially confined fusion (ICF) research.

There has been for some time a variety of techniques available to the experimenter for containerless processing on the ground. These include drop tubes, various levitation devices, and emulsion techniques. While such techniques have their limitations, they have produced a wealth of data and have served to illustrate the advantages of containerless processing. It is precisely the prospect of being able to work in a low-g environment that has attracted considerable attention to applications of containerless processing and has prompted efforts to improve techniques on the ground as part of the development of flight experiments.

### 2.0 Objectives

The objectives of this research activity are to: (1) explore novel applications for containerless processing of glasses and refractory materials by developing state-of-the-art ground-based and flight containerless processing techniques, (2) explore and understand the limitations imposed by the gravitational field, and (3) evolve meaningful flight experiments by identifying where it is necessary to extend processes beyond the limitations imposed by gravity

### 3.0 Justification

The recent attention drawn to containerless processing by the MPS program has served to focus these activities and to stimulate interest in them in a wide variety of research disciplines. In this manner the technology of containerless processing is emerging from isolated experimenters investigating individual research tasks to a concerted multidisciplinary effort to develop better techniques and apply them to a variety of research topics. By developing a strong users community utilizing state-of-the-art ground-based experiments, the applications for containerless technology will grow to exceed the capabilities of ground-based techniques and will provide the rationale for flight experiments.

### 4.0 Background

#### 4.1 Facilities Development

Containerless processing may be carried out on Earth by two basic methods: free-fall facilities and levitation facilities. A free-fall facility, such as a drop tube, offers true containerless and near-zero gravity conditions for a very brief time (at most a few seconds). Levitation facilities support the sample (more or less indefinitely) by means of a force applied without solid contact. Such forces may be electrostatic, electromagnetic, acoustic, aerodynamic, or hydrostatic. One of the disadvantages of using levitation techniques is the fact that the levitation which is unit gravity does require an external force that may influence the experiment by inducing heating, stirring, or other undesirable effects. Also, the applied forces are generally not true body forces but are applied to the surface. Therefore, the sample is still subjected to gravity-driven flows such as sedimentation and natural convection.

Containerless processing in space is essentially a free-fall technique; however, it is necessary to apply low-level levitation forces to compensate for microgravity accelerations and maintain the position of the sample relative to the furnace or experiment chamber. Although such forces may produce some of the extraneous effects encountered in levitation in one-g, the magnitude of such effects can be reduced by several orders of magnitude because of the reduced g-levels.

Of the available levitation techniques, the electrostatic and electromagnetic methods are the only ones that do not require a working medium and, hence, can be accomplished in a vacuum. These are indispensable for certain applications requiring extremely high temperature or ultraclean conditions.

Electrostatic levitation requires charging the specimen and maintaining the charge. Although it is relatively easy to charge an object (either by induction or spraying electrons), it is not a trivial matter to maintain the charge at elevated temperatures. Since intense electric fields are involved, at least in one-g, good vacuum is a necessity, which precludes the use of electrostatic levitation for materials with high vapor pressure. It is well known that there exists no stable configuration of electric fields for maintaining an object at a fixed location. Therefore, a dynamic system is required with a position sensor and a closed-loop servo mechanism to continually control the positioning field.

Electromagnetic levitation is a fairly mature technique for processing metallic samples. Its success depends on the induction of eddy currents in the sample which, in turn, repel the field producing them. This, of course, requires a conductive sample. The technique can be used either with a high vacuum or with an inert gas; however, there can be problems of arcing from materials with high vapor pressures. The system is inherently stable either with a single coil for levitating in one-g, or with a multiple coil arrangement to provide independent three-dimensional positioning control.

Unlike many levitation techniques, the maximum force exerted by electromagnetic induction is not at the end caps or the poles of the sample but at 45 degrees latitude. This helps maintain shape in one-g as the sample melts and is deformed by the combination of gravity and the supporting field. There is a null point in the levitating force along the axis that must be supported by surface tension. This does not present a problem for small samples near their melting points but could be a limiting factor for large samples of high density material with low surface tension. This may also limit the amount of superheat possible because of the decrease in surface tension with temperature.

One undesirable feature of electromagnetic levitation schemes is the sample heating and stirring associated with the levitating process. It is possible to control this to some degree by careful coil design and by gas cooling of the sample so that it is possible to melt and solidify some samples in one-g without physical contact. There is still the question of how the stirring might affect the solidification process.

Considerable effort has gone into the development of acoustic levitation and positioning devices. Such devices utilize acoustic radiation pressure to exert a force on the object. While they do not lend themselves to vacuum operation, they can be used for nonconducting materials, such as many of the glasses and ceramics. The acoustic forces can be intensified by use of a reflector to set up standing waves. The pressure nodes, corresponding to energy minima, are stable levitation points. It should be emphasized that the restoring force is not the first-order pressure fluctuations that occur away from the node; these are alternating forces and time average to zero. There also exist second-order terms that arise from the PV term in Bernoulli's equation and give rise to a time average pressure.

Because these terms are second order, they are considerably weaker than the primary pressures involved in acoustics. However, by use of intense acoustic generators it is possible to levitate solid objects with densities<sup>2</sup> as high as 22 grams/cm<sup>3</sup> in one-g. Considerable effort has been made to develop an acoustic levitation furnace to process samples on the ground. There are several factors that make this extremely difficult and may set limitations on the capabilities of Earth-based systems.

Aerodynamic levitation has been used to some extent to perform containerless processes. By preheating the air and heating the nozzle as well as the sample, temperatures near 1200°C have been achieved. The primary problem with aerodynamic systems is the deformation and instability of the sample as it melts.

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2. The levitation force is proportional to the volume of the sample if the dimensions are smaller than  $\lambda/4$ . For this reason density rather than weight of the sample determines what can be levitated.

#### 4.2 Containerless Processing Experiments

The central reason for wanting to do containerless processing is the elimination of extraneous effects from contact with solid containment walls. The extraneous effects may be chemical reactions with the container, contamination from dissolution of the container in the melt, heterogeneous nucleation at the container wall, wetting and spreading of one component of a two-phase liquid along the container wall, or distortions in shape resulting from physical contact with the container. The experiments and processes that are being developed to take advantage of one or more of these features include physical properties measurements of highly corrosive or high temperature melts, the preparation of ultrapure materials, the formation of unique glasses and alloys, the study of nucleation phenomena and time-temperature-transition (T-T-T) relationships, the rapid solidification of deeply undercooled melts, and the formation of unique shapes such as highly concentric spheres for ICF experiments.

The experiments to determine thermophysical properties of materials at high temperature are of theoretical as well as practical interest. At present very little data are available for materials over 1000°C because of the difficulty of making the measurements. Many systems, particularly molten metals and their oxides, are extremely corrosive and will react with virtually any container. The dissolved components often act as contaminants and alter the properties of interest.

Researchers at Lawrence Livermore Laboratories (LLL) recently have achieved some success in the measurement of high-temperature thermophysical properties of metals by an exploding wire technique in which a high current was passed through a thin wire in a high pressure environment. The current was quenched after the wire had expanded to several times its original diameter, allowing the wire to come to pressure equilibrium with the inert atmosphere. In the few microseconds available before Rayleigh-Taylor instabilities set in, the size and temperature were measured using streak cameras and high-speed multicolor radiometers. Although this method has produced thermophysical data on several metals at temperatures of several thousand degrees, the accuracy is fairly poor, and there is always the question of how close the system was to equilibrium. Also, the technique cannot be applied



to any system other than metallic conductors because it requires a positive coefficient of resistance. Nonmetallic materials become conductors when heated but have negative coefficients of resistance; i.e., electrons are being thermally promoted into the conduction band. This leads to a thermal instability because of nonuniform heating of the wire; i.e., the hot spots become better conductors, have increased current density, and become still hotter at the expense of cooler regions.

Many of the practical systems for which improved thermophysical data are required are nonmetallic. These include various oxides of uranium, plutonium and thorium as well as various forms of concrete, basalt, zircon, etc. These data are required for the reactor safety program in order to evaluate containment criteria in the event of a core melt-down. Other systems of interest are the iron-potassium oxides encountered as electrode slag in coal-fired MHD generators.

The elimination of crucible contamination is beneficial in the preparation of ultrapure materials. It may be possible, for example, to purify certain melts by containerless evaporation if the impurities have higher vapor pressure than the host material. Use of the high vacuum associated with the spacecraft wake would be an additional benefit for such a process. Preparation of oxygen-pure materials would be of technological interest. For example, there is some reason to believe that oxygen impurities in cobalt samarium magnets may be responsible for reverse domain nucleation and may be the limiting factor in the coercive strength of the material. The source of the oxygen is suspected to be the crucible material; therefore, added performance might be derived from containerless melting in an electromagnetic levitator.

Perhaps the most important application for the preparation of ultrapure material could be the production of ultrapure glass for use in optical wave guides. Although extremely high purities have been achieved with quartz using the chemical vapor deposition (CVD) processes currently employed for production of optical fibers, the cost is high and the types of glasses that can be produced are limited. With containerless processing, it may be possible to use a broader range of glasses that are less expensive or have different optical properties but that tend to pick up trace crucible contaminants because of their chemical activity.

Heterogeneous nucleation associated either with the container wall or with contaminants dissolved from the wall limits the formation of an amorphous phase in many materials. It should be possible to extend the glass-forming range of many systems, including some metallic systems, by eliminating heterogeneous nucleation. This could allow sufficient undercooling below the normal solidification temperature to increase the viscosity to the point that the atoms can no longer order into their lowest energy configuration; i.e., a crystalline lattice.

One of the major factors in the formation of amorphous solids is the time-temperature-transition relationship. We know, for example, that many substances can be chilled rapidly enough by splat cooling to form metastable or amorphous phases, but whether or not such phases can be formed by slow undercooling, which would be necessary to process bulk samples, is a matter of conjecture. In normal solidification, heterogeneous nucleation virtually always limits the degree of undercooling that can be achieved. The theory of homogeneous nucleation is not well established and is difficult to test in an unambiguous manner. Some data exist which indicate a serious disagreement with theory. The nucleation and growth of the solid phase in the absence of heterogeneous nucleation sites is obviously an important research area.

If a melt is lowered substantially below its normal freezing point by denying it nucleation sites, solidification, when it does occur, is extremely rapid. As mentioned previously, this rapid solidification may be sufficient to prevent the atoms from rearranging themselves into the lowest energy configuration and may permit the formation of metastable phases with unusual properties, such as the A-15 structure of  $\text{Nb}_3\text{Sn}$  or  $\text{Nb}_3\text{Ge}$ , which are superconductors with the highest known transition temperatures. Containerless solidification appears to be the only method for preparing some of the metastable compounds in bulk form with sizes large enough to study the structure using neutron diffraction technique. As the solidification proceeds into the supercooled melt, the latent heat of fusion is liberated, which causes the material to heat in the vicinity of the interface. This liberated heat raises the supercooled melt to the normal melting point, at the rapidly moving solidification front. Even more spectacular results might be obtained by hypercooling the melt; i.e., cooling below the point at which the

the latent heat of solidification is no longer sufficient to raise the sample to the normal melting point. A spontaneous phase transformation would then be possible with virtually infinite velocity.

The ability to process an object with very weak constraining forces in the virtual absence of buoyancy forces allows the study of a number of processes such as: the growth of crystals from the vapor in the absence of strains and other effects introduced by the support, various droplet phenomena, and the behavior of bubbles in droplets. Of particular interest is the centering mechanisms that operate in the formation of highly concentric glass shells for ICF fuel containment targets. Such shells can presently be made with sufficient precision in sizes up to several hundred microns. These are adequate for present research needs; however, in order to provide fusion power on a practical basis, containment shells up to centimeters in diameter must eventually be produced with a high degree of precision at a low cost. At this time not enough is known about the mechanisms that are responsible for causing the bubble inside the glass sphere to center and produce a concentric shell. A better understanding of this process may indicate a method for scaling up the present process to produce larger size shells. On the other hand, if such a process is not feasible on the ground, the shells could be manufactured in space.

## 5.0 Experiment Status and Remaining Issues

### 5.1 Facilities Development

#### 5.1.1 Drop Tube

A 34 m drop tube is in operation at MSFC which provides 2.6 sec of free fall. During this time molten droplets up to several millimeters in diameter can be solidified.

Several modes of melting are available. For high-temperature refractory metals, the sample can be mounted on a sting of like composition and melted by electron bombardment. This, of course, requires a vacuum; therefore, the sample must solidify by radiating its latent heat of evaporation. Since the effectiveness of radiative cooling varies as  $T^4$ , only high melting point samples

(> 2500°C) can be solidified in this manner. Also, the degree of superheat is limited a few hundred degrees above the melting point because only surface tension suspends the droplet after it has melted. This makes it difficult to homogenize composite mixtures or to heat an immiscible system above its consolute temperature.

Other heating systems are available that can work in a low pressure He environment. The use of such an environment provides effective forced convective cooling without adding significantly to the drag force. This allows lower temperature materials to be solidified under approximate free-fall conditions. An elliptical arc imaging furnace (Costello furnace) focuses a xenon arc on the sample placed at the other focus. This technique can melt pendant drops up to 1400°-1500°C, the limiting factor being the strong convective cooling associated with the sample insertion port. Again, the superheat is limited by the surface tension suspending the pendant drop.

An alternative scheme which can provide some degree of superheat for melting and homogenizing is a capillary tube furnace. A quartz capillary is heated by a tungsten coil, and the sample is ejected by a short burst of pressure. This technique is limited by the operating temperature of quartz. Also, this does not provide for containerless melting and cannot be used for systems that are highly reactive in the melt.

In order to provide for containerless melting and solidification of materials that require high degrees of superheat for homogenization, it would be desirable to couple a large (15-25 kW) electromagnetic levitator to the drop tube. The induction heating would be sufficient to process most metals (i.e., Fe, Ni, etc.). Auxiliary e-beam heating would allow the processing of refractory metals, such as W, Ta, Zr, etc., and their alloys.

One disadvantage of a drop tube compared to levitation processing is the difficulty in observing the sample as it solidifies. It is quite essential, for example, to know the degree of undercooling achieved before solidification took place. This requires extensive instrumentation within the tube to observe and record the "blink" or flash of light associated with release of the latent heat.

Early techniques recorded this photographically, but these are inadequate for routine operation, especially when it is not known a priori where the sample will be in the tube when it solidifies. A series of infrared detectors that cover the tube and an automated recording system have been installed to provide this coverage.

#### 5.1.2 Single-Axis Acoustic Levitator

Two basic types of acoustic levitators have been developed for flight. The single-axis device is similar to the system used for levitation in one-g. It uses a high-Q driver with a single frequency (i.e., the resonant frequency of the driver). No attempt is made to tune the furnace cavity or compensate for the change in wavelength as the furnace temperature changes. In fact, the furnace walls are made as nonreflective as possible. The stable energy is created by the interference between the incoming wave and the reflected wave, and this well simply moves relative to the reflector as the wavelength changes with temperature. The depth of the well, hence the stability, is enhanced if the reflector is tuned (i.e., an integral number of half wavelengths from the driver), but this is not critical.

Sample capture and stability have been demonstrated for the single-axis levitator in low-g using KC-135 aircraft. However, in a recent SPAR flight, after a successful capture, the sample appeared to drift radially out of the well at about the time the sample melted. It is believed that the acoustic level was too low to provide sufficient restoring force to overcome vehicular accelerations. A second SPAR attempt is being readied which will have an improved acoustic driver.

Considerable effort has gone into the development of a ground-based acoustical levitator processing capability. Attempts to spot heat a levitated sample using a CO<sub>2</sub> laser have been unsuccessful because of the interaction of the convective plume arising from the hot sample with the standing wave pattern. This severely distorts the energy well and results in immediate expulsion of the sample.

An isothermal furnace was built with the acoustic driver located just below the heated cavity and coupled through a port. As the temperature is increased, the air

density decreases, the wavelength becomes longer, and the viscosity of the gas increases--all of which conspire to reduce the levitation force as approximately the inverse cube of the temperature. The use of focusing drivers and reflectors, higher pressures, and dense gases (such as Xe) restored some of this loss. However, it was then found that the sample temperature was substantially lower than the wall temperature. This is caused by acoustic streaming of cooler gas from the acoustic driver face which, because it is an Al alloy, must be maintained below 600°C. Experiments with other higher temperature-driven materials have not yielded satisfactory acoustic performance. This may be a fundamental limit on the capabilities of acoustic containerless processing on Earth.

#### 5.1.3 Three-Axis Acoustic Levitator

The three-axis acoustic levitator has also been under development for a number of years. In this device three mutually orthogonal drivers produce a three-dimensional sound field in a tuned cavity, exactly one-half wavelength in each dimension. This creates essentially a spherical energy well in the center of the cavity which is the only stable region. By varying the phase or intensities of the drivers, the sample can be manipulated by inducing oscillations or rotations.

Since the three-axis system requires tuning of each driver, it is necessary to introduce an automatic frequency control to compensate for the wavelength change as the temperature is varied. This requires the use of high-compliance drivers that can operate over a range of frequencies.

The system has been successfully demonstrated at ambient temperatures in a number of KC-135 flights and a SPAR flight and has proven to be a valuable technique for the study of dynamics of fluid droplets. There remains the question of operation at high temperatures. If the system is operated with the walls at ambient temperature by heating the sample, there will be significant thermal gradients in the surrounding gas. This will alter the local sound velocity and could destroy the resonant condition. Therefore, it may not be possible to operate at high temperatures with cold walls.

If this is the case, high-temperature operation must be accomplished by heating the entire cavity so that the acoustic positioning occurs in a more or less isothermal

gas. This poses a difficult design problem in fabricating a high-compliance driver that can withstand the high cavity temperatures (1200°-1600°C). One possible approach would be to locate the driver remotely and use an acoustic wave guide to couple the sound energy into the cavity. However, this raises the possibility of shock formation in the wave guide and the question of how effective such a coupling might be.

One of the desirable features of the three-axis system is the ability to rotate the sample. This can be accomplished by altering the phase of two of the drivers so that the sample sees a rotating pressure field. Such rotation has been demonstrated in the laboratory using low-density solid spheres and on a SPAR flight using liquid droplets. One of the remaining questions is whether it is possible to prevent rotation of an object while it is being processed; e.g., asymmetrically heated. It is known that in the single-axis device, in which there is no effort to control rotation, some samples spin rapidly while others do not. The reason for this behavior is not clear but must involve some asymmetry in the sample or in the sound field. Maintaining rotational control is not a developed technology.

#### 5.1.4 Aerodynamic Levitation

Aerodynamic levitation using a jet of air from a carefully designed nozzle has been used by some workers to suspend highly reactive samples in order to study various chemical reactions. By heating the nozzle and the air and by radiatively heating the sample, temperatures in the range of ~1000°C can be achieved. Small (millimeter size) metallic and glass samples have been melted and solidified by this technique, although control of samples as they become liquid is very difficult, and the sample tends to touch the nozzle as it deforms. If improved nozzle design can prevent this occurrence, the aerodynamic levitation facility could become a very useful tool for processing unique glasses or for obtaining T-T-T information for various systems in the absence of heterogeneous nucleation.

#### 5.1.5 Electromagnetic Levitation Containerless Melting and Solidification

A 10 kW electromagnetic levitator facility for containerless melting and solidification (COMAS) is currently in operation. By careful coil design, which

maximizes Grad B/B, samples can be levitated with a minimum of heating. This allows the power to be reduced after the sample has been melted so that solidification can occur without contact. The addition of a quench gas extends the range of materials that can be processed in the COMAS facility.

Numerous samples ranging from Al-In to Ni superalloys have been melted and solidified. Undercoolings approaching 12 percent of the melting temperature have been measured, thus indicating that the intense stirring associated with the levitation process does not prevent undercooling. However, it does appear that the degree of undercooling possibly diminishes as the current is increased. This is evidence for some sort of dynamic nucleation.

Fine dispersions of In in an Al matrix were obtained by containerless solidification of this monotectic alloy. One sample that inadvertently touched the levitator coil during solidification had very little In in the interior. The In wets the copper coil very well, and practically all the In was wicked out of the Al in spite of the stirring from the levitation process. This indicates the importance of surface tension capillarity in the decomposition of monotectic systems.

In other tests it was demonstrated that samples could be melted and dropped with a spread of 5 mm in a distance of 1 m. This indicates such a system could suspend superheated droplets and drop them through a 15.24 cm (6 in.) drop tube more than 50 m long.

A 25 kW induction heater has been obtained from surplus and is in the process of being refurbished and modified to serve as a larger containerless processing facility. Methods for obtaining higher temperatures are being investigated.

#### 5.1.6 Electrostatic Levitation

A quadrupole configuration electrostatic levitator has been constructed and demonstrated. Small charged objects can be suspended between four horizontal rods which produce time-varying fields to maintain stability. Particles can be moved parallel to the rods by application of d.c. fields. Such devices could be used for manipulating and positioning glass shells during processing.



Work has been initiated on a multi-axes positioning device using d.c. fields with active feedback position control.

#### 5.1.7 Remaining Issues

1. The question of whether stable acoustic positioning can be accomplished in low-g with large sustained gradients between the sample and the walls needs to be settled. This will determine what can and cannot be done in acoustic containerless systems.

2. Techniques of rotational control need additional development. This includes prevention of rotation as well as producing rotations about multiple axes if required.

3. The amount of stirring produced in the sample by the acoustic field must be assessed together with possible effects on nucleation and solidification.

4. Techniques for maintaining stable suspension of liquid material at high temperatures in an aerodynamic levitator are required. Limitations on droplet size must be established and understood.

5. Aerodynamic positioning/levitation for use in low-g may be a simpler alternative to acoustic positioning. This deserves additional research to determine the possible advantages and pitfalls.

6. Samples melted and solidified in a containerless aerodynamic or electromagnetic levitation system should be compared with those processed under free fall in order to examine the effects of the levitation process and to establish limitations of the technique.

#### 5.2 Containerless Processing Experiments

##### 5.2.1 Measurement of Thermophysical Properties

##### 5.2.1.1 Thermophysical Properties of Tungsten (Margrave)

This research is directed toward the measurement of the thermophysical properties of tungsten at very high temperatures. Samples are suspended containerlessly by an electromagnetic levitator. Additional heat is supplied by electron bombardment. Temperatures are measured by pyrometers. Heat capacities are determined from cooling curves, and total enthalpy is obtained using a drop calorimeter.

#### 5.2.1.2 Thermochemical Properties of K-Fe Oxides (Parker)

The main objective of this study was to explore the limitations of ground-based techniques for measuring thermochemical properties of oxide systems that are highly corrosive in the melt. The system chosen was  $K_2O$  - iron oxide -  $SiO_2$ . This system is of importance to MHD generation because these oxides are major components of seed and coal slag.

The first portion chosen was the  $KFeO_2$ - $Fe_2O_3$  binary. It was found, contrary to expectations, that Pt could be used to contain this material at greater than  $1500^\circ C$ , provided the Fe remained in the 3+ state.

#### 5.2.1.3 Development of Containerless Calorimetry Techniques (Colwell)

This is a theoretical investigation of various radiometric measurement techniques that can be employed to obtain thermophysical properties of a levitated sample. In particular, complications imposed by thermal gradients within the sample have been investigated, and methods of obtaining thermal conductivities have been worked out for certain conditions.

#### 5.2.1.4 Remaining Issues

The primary remaining issue is whether low-gravity operation will be required to determine certain high-temperature thermophysical properties. This can only be established by making exhaustive attempts to develop various levitation techniques, especially electromagnetic and aerodynamic, to their maximum potential and attempt to make such measurements. This will establish the limitations of the available ground-based techniques, drive out the requirements for a spaceborne facility, and establish an active cadre of experimenters to utilize such a facility.

#### 5.2.2 Preparation of Ultrapure Materials

##### 5.2.2.1 Ultrapure Glass for Optical Wave Guides (Mukherjee)

In order to process an ultrapure glass in space, extreme care must be devoted to preparation of the starting material. Preparation from a melt will often

C-2

introduce the contaminants that one goes to space to avoid. Also, homogenization of a mixture of components in space may be difficult because of the absence of convective stirring. For these reasons glass preparation from sol-gels may be desirable. This research effort is devoted to the development of gel techniques for forming multicomponent glasses, the development of ultrapure gels, and the characterization of the gels and the glasses formed by the gel process.

#### 5.2.2.2 Preparation of Ultimate Coercive Strength CoSm<sub>5</sub> (Das)

The objective of this effort is to investigate the role of oxygen as a contaminant in nucleating reverse magnetic domains in the CoSm<sub>5</sub> system. Cobalt/rare-earth systems have the best magnetic properties of any materials known today; however, their coercive strength is only approximately 30 percent of the theoretical maximum. If this could be improved, there would be a significant benefit in systems requiring very stable magnetic fields, such as instruments and inertial navigational platforms.

Because this material is highly corrosive in the melt it is conjectured that oxygen is being picked up from the silica or alumina crucibles.<sup>3</sup> Preliminary studies are attempting to relate coercivity to oxygen content of CoSm<sub>5</sub> prepared by different techniques. This has not proved to be straightforward. Attempts will be made to prepare CoSm<sub>5</sub> directly from the pure materials using containerless electromagnetic melting.

#### 5.2.3 Formation of Unique Glasses and Alloys

##### 5.2.3.1 Preparation of Galia-Calcia Glasses (Happe)

Many potential glass systems are difficult to form because of the presence of heterogeneous nucleation sites that arise from contaminants dissolved from the container wall or from the container wall itself. By avoiding such container effects, it is hoped that the potential glass

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3. CoSm<sub>5</sub> reacts with other crucible materials such as BN. Skull melting cannot be used because of the high thermal gradients, which necessitates a large degree of superheat at which the vapor pressure of Sm is a problem.

formers can be undercooled to such an extent that the increase in viscosity will prevent the atoms from ordering into a crystalline phase. This technique may be able to produce new materials with unique optical properties or improved laser host glasses.

Galia-calcia represents one of the materials of interest for containerless processing. A SPAR experiment with a galia-calcia-silica sample has been flown in the single-axis levitator furnace. The silica was added on the first flight to improve the glass-forming capability so that the heating and cooling of the sample could be evaluated in the event that the galia-calcia failed to form a glass for whatever reason. The acoustic driver produced a lower than expected acoustic well, and the sample drifted into the containing cage as it melted. One encouraging result was the fact that practically no bubbles were trapped in the sample, which has been considered to be one of the major problems with processing glasses in a low-g environment.

#### 5.2.3.2 Preparation of Unique Optical Glasses (Happe)

This is an extension of the SPAR experiment described previously. By using a modified single-axis levitator furnace with automatic sample exchange, a variety of samples can be processed on a MEA flight.

#### 5.2.3.3 Preparation of Metal-Oxide Glasses (Weinberg)

This effort is directed toward development of sample preparation techniques for reluctant glass-forming systems to be containerlessly processed in space. Of particular importance is the avoidance of impurities during the preparation of the starting material that could serve as nucleation sites or as absorption or scattering centers. Elaborate characterization techniques are being developed to evaluate the preparation techniques and the glasses that are formed.

#### 5.2.3.4 Glass Fining in Space (Weinberg)

In the absence of Stokes bubble rise, glass fining in space becomes more difficult. Certain chemical fining agents may be introduced to aid in bubble dissolution. Such agents are also used in commercial glass processing on Earth to hasten the fining process and reduce the

energy requirements for glass processing. A space experiment is being developed to evaluate chemical fining techniques for space processing of glass as well as to study the action of commercial chemical fining agents without the complications from Stokes rise.

#### 5.2.3.5 Solidification of Miscibility Gap Alloys (Gelles)

A portion of the experiment to investigate the separation mechanisms involved in the solidification of monotectic alloys (see Section 5.3.1 in the chapter on Solidification of Metals, Alloys, and Composites) will be performed in either the single-axis acoustic levitator furnace or in the electromagnetic levitator. The objective will be to investigate the influence of surface wetting and capillarity, which seems to be an important factor in causing the observed separations in the absence of a container wall.

#### 5.2.3.6 Remaining Issues

The major issues in containerless glass formation are:

1. The avoidance of impurities in the sample preparation. Such impurities, if present, could act as nucleation sites and limit the glass-forming capability of the system. Several studies are being devoted to this problem.

2. Control of bubbles in the melt. Since bubbles do not rise at Stokes flow in low-g, their suppression and/or removal must be given special consideration. Two studies are addressing this question (see Sections 5.2.3.3 and 5.2.6.3 in this chapter).

3. Size effects in containerless processing of glasses. It is well established that small samples can be undercooled sufficiently to form glasses when equilibrium solidification favors a crystalline structure. However, larger samples require considerably longer times to cool. Since crystalline transitions are favored by longer times, there may be a limiting size for which containerless processing offers any advantage. Also, large size samples will tend to contain more potential heterogeneous nucleation sites. These size limits must be established (see the following Section 5.2.4).

#### 5.2.4 Time-Temperature-Transition Relationships

No work in this discipline is currently being sponsored by the MPS program.

##### 5.2.4.1 Remaining Issues

An active program using containerless techniques to study time-temperature-transition relationships in the absence of heterogeneous nucleation should be initiated to determine whether homogeneous nucleation can be achieved and to establish the experimental limitations it imposes on undercooling.

#### 5.2.5 Rapid Solidification from Deep Undercooling

##### 5.2.5.1 Formation of Metallic Glasses (Lord)

See Section 5.4.1, in Solidification of Metals, Alloys.

##### 5.2.5.2 Nucleation and Growth in Glass-Forming Alloys (Turnbull)

See Section 5.4.2, in Solidification of Metals and Alloys, and Composites.

##### 5.2.5.3 Formation of Metastable Peritectics in a Drop Tube (Lacy)

See Section 5.4.3, in Solidification of Metals, Alloys, and Composites.

##### 5.2.5.4 Remaining Issues

1. It must be demonstrated that it is possible at least in principle to undercool larger objects to the point where solidification is rapid enough to produce the desired microstructures.

2. The possibility of seeding an undercooled melt to produce the desired phase should be considered.

## 5.2.6 Glass Shell Formation

### 5.2.6.1 Containerless Processing Technology (Wang)

A series of SPAR experiments is being carried out in the three-axis levitator to gain experience and demonstrate various technologies required for the perfection of containerless processing. Drop capture, induced oscillation, and rotation were demonstrated on SPAR VI. A similar experiment on SPAR VII will deploy two droplets to investigate coalescence and mixing.

### 5.2.6.2 Bubble Centering Mechanisms in Containerless Processing (Wang)

Following preliminary experiments in KC-135 aircraft, in which it was demonstrated that a bubble in a thin-walled water sphere could be centered by inducing certain oscillations, a SPAR experiment has been developed in which an air bubble will be injected into a drop and subjected to various manipulations to study bubble centering mechanisms. In addition to oscillations produced by pulsing the sound intensity, rotation will be induced by altering the phase of the sound source. Finally, the bubble will be expanded by adiabatic decompression.

These experiments are a prelude to later experiments designed to study the production of fuel containment shells for the ICF program.

### 5.2.6.3 Control of Bubbles in Low-g Glass Processing (Subramanian)

The objective of this proposal is to understand and develop techniques for manipulating bubbles in glass melts for the purpose of their removal or for producing concentric glass shells for ICF applications. An extensive theoretical analysis of flows induced by various thermal effects, including spot heating, has been developed.

The experiment has been approved for flight development. Difficulties have been encountered in accommodation of the experiment since it is not clear how orientation control can be maintained for the sample while it is positioned containerlessly and spot heated.

### 5.2.6.4 Production of Glass Microspheres for Fusion Targets (Nolen)

The objective is to use MPS-developed capabilities such as levitators, low-g aircraft flights, and

eventually spaceflight experiments to develop a better understanding of the bubble formation and centering in the current production methods. It is hoped that such understanding can be used to improve production techniques and extend the possible range to larger sizes that will ultimately be required for fusion work. If it is shown that current production cannot be scaled up to larger sizes for fundamental reasons, production of the larger shells in space will be seriously considered.

#### 5.2.6.5 Upgrading of Glass Microballoons (Dunn)

An alternative technique to the blowing techniques used by KMS Fusion (KMSF) and LLL for producing glass shells for ICF work is to form short cylinders by sealing off sections of capillary tubes, spheroidizing them by levitation, and rotating them randomly using an aerodynamic levitator. Various aerodynamic levitators have been developed for this purpose, and tests are in progress.

#### 5.2.6.6 Production of Laser Fusion Targets (Wang)

This effort, co-sponsored by the Department of Energy (DOE) through LLL, is designed to utilize NASA's containerless processing technology to study the problems associated with producing the larger size, highly concentric glass shells eventually needed for the ICF program.

#### 5.2.6.7 Remaining Issues

1. The central issue is the future of ICF and whether glass shells will continue to be used for fuel containment.
2. The size, thickness, and allowable deviations required for containment shells are still in a state of flux.
3. Apparently some centering mechanism is operating in the current ground-based processes. If this mechanism can be elucidated by space experiments and exploited in improved ground techniques, this would be a significant contribution.



## 6.0 Assessments and Recommendations

### 6.1 Facilities

#### 6.1.1 Drop Tube Development

The drop tube at MSFC has proven to be a highly successful facility and has attracted considerable attention. Several requests have been received from industry to process samples under the newly instituted Technical Exchange Agreements. The increasing demands for testing and the fact that the space available in the present locale severely restricts the types of heating and levitation that can be employed strongly support relocation of the drop tube and construction of a second facility. A location near the present drop tube has been identified that would allow adequate working space and could extend the tubes length by 16 m. This would increase the free-fall time to 3.2 sec (23 percent increase). Another alternative would be to locate the new drop tube in the vertical test stand and extend the length by some 65 m. This could increase the time to 4.5 sec (75 percent increase).

#### 6.1.2 Acoustic Levitation

It appears that the development of ground-based acoustic levitation capability has reached a point of diminishing return unless an unforeseen breakthrough in technology occurs. Emphasis should be given to understanding flight problems, such as resonance conditions in the single-axis interference technique, control of sample rotation, sample stirring, etc. A major question that should be addressed at the earliest possible opportunity is the method of sample heating. This will have profound effect on the application of acoustic levitators. For example, if they must be heated isothermally to avoid thermal gradients in the acoustic well, sample heating is limited to the operating temperature of the walls, and quench rate will be difficult. If the sample can be separately heated with cold walls, much higher temperature can be obtained, extremely rapid quenching can be achieved, driver problems can be vastly simplified, and chamber cross contamination can be virtually eliminated.

A preliminary set of experiments should be conducted on a KC-135 using spot heating on both single-axis and three-axis devices. More sophisticated experiments should be conducted on SPAR and later on Shuttle flights.

### 6.1.3 Aerodynamic Levitation

This technique holds considerable promise as a ground-based method for melting and solidifying small nonconductive samples and as a flight alternative to acoustic levitation, particularly if it proves unfeasible to maintain a superheated sample in a stable acoustic well.

More effort should go into nozzle design to maintain stability as the sample melts. If this can be accomplished, many of the processes that were originally considered for study with the ground-based acoustic levitator could be accomplished by aerodynamic levitation.

In such studies, priority should go to the study of the formation of microspheres for ICF targets from the frit. In normal production, this process takes place in the tube furnace and is difficult to observe. Knowledge of how this process takes place and the ability to observe directly how an individual piece of frit evolves into a particular glass shell are important keys in understanding target shell production.

Such a facility would also be ideal for studying glass formation, phase diagrams, T-T-T diagrams, etc.

### 6.1.4 Electromagnetic Levitation

The COMAS has also proven to be a valuable capability for studying the containerless processing of metallic materials. The present facility is limited in its ability to heat much above 1500°C. Unfortunately, this is below the minimum temperature at which drop tube samples can be deeply undercooled and solidified. It would be most useful to be able to compare such samples that have been electromagnetically levitated with those that have been solidified in free fall to determine the role of intense stirring in the solidification process.

The upgrading of the facility to 25 kW should be a substantial help. The addition of auxiliary heating such as e-beam or CO<sub>2</sub> laser should also be considered to achieve temperatures in excess of several thousand degrees. The addition of a high-speed, multicolor pyrometer and a gulp calorimeter will enable exploratory measurements of thermophysical properties.

Attention should also be given to development of techniques for suspending and heating nonconductive samples until they reach a temperature at which sufficient thermal electrons are available to raise the sample conductivity to the point where it can be levitated electromagnetically. Since most of the materials of interest from the measurement of thermophysical properties point of view are nonconductive, this is an important technology that must be demonstrated.

Finally, a technology that also needs to be developed for the study of controlled solidification is the insertion of a seed into an undercooled melt. This would also be valuable in the study of the role of surface wetting in the decomposition of immiscible alloys.

#### 6.1.5 Electrostatic Levitation

Electrostatic levitation appears to be a particularly useful technique for positioning large objects in a high vacuum when it is important to avoid stirring produced by electromagnetic levitation or when dealing with nonconductive materials. Substantial progress has been made in demonstration of this technique in neutral density buoyancy tanks. Priority should be given to the demonstration of this technique in a low-g aircraft.

The use of electrostatic positioning arrays is also promising for handling and manipulating a large number of small objects. No direct application for this technology has been identified, but it appears to have several potentially important uses as the program matures.

### 6.2 Containerless Processing Experiments

#### 6.2.1 Thermophysical Properties Measurements

This appears to be a fruitful area of research for containerless technology on the ground as well as in space. Facilities, such as the electromagnetic and airjet levitators, exist that are capable of suspending objects heated to high temperatures. These facilities need to be upgraded by adding additional heating capabilities, either in the form of E-beam, CO<sub>2</sub> laser, or arc imaging, and development work on instrumentation should be initiated. This will serve as a breadboard for a later space experiment and as a proving ground for heating techniques,

thermophysical measurements, sample handling, automatic exchange, etc. In addition, such a facility should serve to stimulate interest in the scientific community by advancing the current state of the art in containerless measurement technology and by providing potential investigators with the best available ground-based apparatus to make their measurements. This will develop an active users community and provide a natural mechanism for developing flight experiments when the need for more levitation capability becomes evident.

#### 6.2.2 Ultrapure Materials

The work currently in progress is a start in this important field, but additional work needs to be initiated in identifying the requirements and processing techniques for ultrapure materials. Of primary importance is a wider variety of ultrapure glasses for use in optical waveguides. The preparation of uncontaminated starting material is, of course, crucial to the preparation of such glasses, and the sol-gel process appears to lend itself to this application. However, other, possibly more promising, systems need to be explored in addition to the  $\text{Na}_2\text{O}-\text{B}_2-\text{SiO}_2$  system presently under investigation. Consideration also needs to be given to how such glasses could be produced into optical fibers without contamination.

Another possible application for ultrapure glasses is in improvements for high-power laser systems. Some work should be initiated to investigate the effects of impurities in existing components to determine what advantages might be obtained if purer materials could be made available.

There is also considerable interest in the preparation of ultrapure metals as discussed in the chapter on Vacuum Processing. Containerless positioning techniques may be required in conjunction with the low-g and ultrahigh vacuum environment in order to carry out certain of the processes envisioned. For example, electromagnetic levitation would be useful for carrying out vacuum melting operations for removing impurities that are more volatile than the host material. An early demonstration of such a technique is highly recommended.

### 6.2.3 Preparation of Unique Glasses and Alloys

The ability to form unique glasses is perhaps one of the most exciting aspects of containerless processing. The approach taken by Happe is a good first start, but several improvements and some longer range planning are badly needed in this area. First of all, the laser melting used to screen various candidates employs a sting to support the melt. This is a possible source of contamination that could be avoided by use of an aerodynamic levitation technique. Also, the preparation of the starting material is extremely critical because crucible contaminants can easily enter unless a technique such as the sol-gel process being developed by Weinberg is used to avoid melting of the starting material. A closer coordination between these efforts would be highly desirable.

Bubble formation is a potentially serious problem in low-g containerless processing. Chemical fining techniques, such as those being investigated by Weinberg, as well as the thermocapillary techniques for controlling bubbles will be required. The chemical fining is particularly attractive because it offers a method for actually removing the bubbles, whereas the thermocapillary techniques being investigated by Subramanian and by Wilcox (see Section 5.5.3, Fluids and Chemical Processes) only control the position of the bubble. A possible serious concern that must be addressed is the possibility that the addition of chemical fining agents may adversely affect the optical characteristics or glass-forming properties of the material.

The influence of container wall effects on the separation of miscibility gap alloys (see chapter on Solidification of Metals, Alloys, and Composites) is of fundamental interest to many glass systems that exhibit phase separation as well as to the preparation of uniformly dispersed monotectic alloys. Containerless experiments will serve to elucidate these effects.

For most practical applications, much larger sizes than the centimeter diameter samples presently envisioned will be required. Not only will such sizes require new concepts in levitation technology, but many encounter some fundamental limitations imposed by the bulk of the sample. For example, as the size increases, the ability to extract heat, hence the cooling rate, is limited by size and conductivity of the sample. Therefore, it may not be possible to chill the sample rapidly enough to avoid the

crystallization region in the time-temperature-transition (TTT) diagram. Also, if the potential nucleation sites (homogeneous as well as heterogeneous) increase as the bulk of the sample, it may not be possible to avoid nucleation of large samples even though wall effects are eliminated. Fundamental work on nucleation and TTT diagrams is crucial to the extension of containerless processing to bulk material.

#### 6.2.4 Time-Temperature-Transition Relationships

Although there is no direct activity in this area at present, this is an excellent research opportunity that should be pursued as part of the containerless processing program. Some of the undercooling work and the nucleation work of Weinberg, Turnbull, and Lacy are related to this potential application but do not take full advantage of the capabilities for suspending a sample for long periods of time at a given temperature. This ability would allow the determination of the probability of homogeneous nucleation events producing nuclei of critical size. It appears that fundamental contributions could be made to the science of homogeneous nucleation by such techniques. One of the world's leading authorities in this area, Dr. Perepezko, has expressed interest in such studies but has not submitted a formal proposal. Professor Turnbull's work could also utilize this capability but at present is not moving in this direction. An unsolicited response to the Application Notice (AN) has been submitted by a USRA visiting scientist, Dr. Ethridge. The proposal is still undergoing peer review.

#### 6.2.5 Rapid Solidification from Deep Undercooling

These experiments are discussed in the chapter on Solidification of Metals, Alloys, and Composites.

#### 6.2.6 Glass Shell Formation

The use of low-g to study the process of glass shell formation, bubble centering, and possibly even the eventual production of large concentric shells is an excellent example of the contributions that the MPS program can make to solve important technological problems. This highly active program involving neutral buoyancy experiments, aerodynamic drop tubes, KC-135 experiments, and SPAR flights is jointly sponsored by NASA and the

Department of Energy and provides a cooperative research effort between Jet Propulsion Laboratory (JPL) and Lawrence Livermore Laboratories. This effort has already made important contributions to the understanding of the mechanics involved in bubble centering and promises to provide the necessary technology for the eventual scale-up of the containment shells required for power ICF reactors.

The NASA-sponsored work at KMS Fusion, has resulted in a detailed understanding of the chemistry involved in the glass prepared by the sol-gel process. Of particular interest is the observation of the formation of glass shells from the starting material. The aerodynamic levitator system developed by Bjorksten Laboratories appears to be capable of suspending small particles of the frit produced from the dried gel and heating through the glass formation temperature.

Because of the recent progress by LLL and KMSF in shell production, the method of producing shells by suspending and rotating capillary tubes is of less importance. Therefore, it is recommended that the Bjorksten work be redirected toward studying the process of shell formation as discussed previously. Of particular interest is the adaptation of aerodynamic levitation techniques to low-g use.

Similarly, it now appears that thermocapillary forces are not the primary mechanism for bubble centering. It is therefore recommended that the work of Subramanian be directed toward control of bubbles in glass formation with less emphasis on fabrication of concentric containment shells.

### 6.3 Availability of Flight Hardware

At present there are three types of equipment available for performing containerless processing in space. These devices, developed for SPAR, are: (1) an electromagnetic levitation facility, (2) a single-axis levitation furnace, and (3) a three-axis ambient temperature acoustic levitator.

The electromagnetic facility has flown on two SPAR flights. The system was disassembled for modification with the intent of adding a cold gas quench system to

improve the quench rate. The system could be reassembled with or without the quench gas system and flown in SPAR or in MEA.

The system can levitate and heat samples up to 1 cm diameter to 1400°C. The diagnostic instrumentation consists of a 16 mm camera and a radiometer. Most of the sample is occluded by the coil, which limits the view and prevents automatic sample exchange. Some modification of this may be possible.

Since thermophysical properties measurements can be made repeatedly on the same sample, this facility might be useful in its present configuration.

The single-axis acoustic levitator can melt and solidify 1 cm diameter samples at temperatures up to 1550°C. It contains a 16 mm camera for diagnostics. Rapid quenching is possible by means of the insertion of a cooling shroud into the chamber, which approximates radiation cooling.

The system has been flown once, and the sample was lost from the acoustic well approximately 30 sec after it was successfully deployed and captured. A failure analysis revealed that the sound intensity was lower than anticipated and that a resonance condition may have occurred as a result of wall reflections which expelled the sample from the well. Tests are underway to establish the cause of the failure and to provide a fix.

At present, the levitator can only accommodate a single sample. A multiple-sample turret could be adapted fairly easily to the existing configuration. Since the experiments that would use this facility require the processing of a number of samples, multiple-sample capability would be essential to take advantage of the long time available in Shuttle flights.

The three-axis acoustic levitator can process multiple liquid samples at ambient temperature. The processing capability consists of oscillation and rotation of droplets, deployment and merging of multiple droplets, and the injection of air bubbles into the droplets. No heating or cooling capabilities exist, nor do provisions for deploying and retrieving solid samples; however, the feasibility of adding such capabilities should be explored.



Diagnostics consist of a 16 mm camera with mirrors providing three-axis orthogonal viewing.

#### 6.4 Working Group Activities

The containerless processing effort is supported by two working groups. One, under the direction of Dr. Doremus, is primarily concerned with containerless processing of glasses; the other, under the direction of Dr. Oran, is primarily concerned with applications of electromagnetic levitation. Both groups have been extremely successful in stimulating interest in containerless processing and are responsible for bringing many new ideas and outstanding scientists into the program.

The electromagnetic working group has developed some preliminary concepts of a facility devoted primarily to thermophysical measurements and has estimated the requirements for such a facility. This information together with the scientific rationale and justification will be used to develop a new start activity for 1982.

This working group has also recommended the development of a precursory experiment using the existing SPAR EM levitator to fly either on SPAR or MEA to demonstrate the techniques for containerless measurement of thermophysical properties. An unsolicited proposal has been prepared and submitted for comments.

## ULTRAHIGH VACUUM PROCESSES

## Ultrahigh Vacuum Processes

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## Ultrahigh Vacuum Processes

### 1.6 Introduction

The potential for using the high vacuum in the wake of an orbiting spacecraft has been recognized for a number of years. Theoretically, this vacuum environment should exceed the best vacuum chambers on Earth and will allow processes to be carried out that involve large quantities of heat and/or gas release and still maintain an ultrahigh vacuum. This unique combination of high vacuum capability with high heat rejection and high pumping speed should have research and industrial applications.

### 2.0 Objective

The objective is to develop scientific and industrial applications for the use of the unique vacuum capabilities afforded by the wake of an orbiting vehicle. A logical approach is to: (1) measure the vacuum environment in the wake of the Shuttle, (2) use the resulting data to determine the additional facilities required to achieve the desired vacuum levels, (3) perform selected experiments to demonstrate the use of space vacuum, and (4) develop an active users community.

### 3.0 Justification

The use of space vacuum processing is a theoretically sound concept but has not been experimentally demonstrated. Several possible applications have been proposed. A demonstration of the utility of space vacuum processing is expected to stimulate scientific and industrial interest in this unique capability.

### 4.0 Background

#### 4.1 Vacuum Environment Definition

Because the orbital velocity of a spacecraft in near-Earth orbit is several times faster than the average molecular velocity of the residual atmosphere, the spacecraft literally outruns these molecules. An observer looking in the wake direction would see practically no heavier molecules, such as atomic or molecular oxygen or nitrogen. Only the lighter molecules, such as hydrogen or

helium, have a small probability from the tail-end of Maxwell-Boltzmann distribution to overtake the vehicle. Calculations indicate that this flux is comparable to  $10^{-14}$  to  $10^{-15}$  Torr.

Two factors can significantly degrade the vacuum environment behind such a wake shield. The first is the outgassing from the shield itself; the second is molecular scattering from molecules released from the spacecraft or from the sample. Such molecules will have thermal velocities which are small compared to the spacecraft velocity, and they have mean free paths that are long compared to the dimensions of the spacecraft. They can, however, act to scatter atmospheric components into the sample region.

The outgassing from the shield material can be controlled by the appropriate choice of materials, cleanliness, and bakeout. A number of tests have been conducted in the laboratory on various materials. It appears that either aluminum or stainless steel can be used if proper passivation techniques are used. Also, it appears that it is unnecessary to launch such a shield in a pre-evacuated configuration and that on-orbit bakeout is probably not required.

Obtaining accurate estimates of the vacuum levels obtained in space is more difficult. A number of studies, including an elaborate Monte Carlo computation, have been conducted to estimate the vacuum environment behind a shield connected to the Shuttle. There are several unknowns which preclude accurate estimates at this time. First, the outgassing rates from the Shuttle are essentially unknown. Second, the scattering cross sections between the outgassing molecules and the atmospheric components are unknown. The latter is particularly critical since the probability of an energetic atmospheric molecule being backscattered in a collision is highly dependent on the energy loss in the collision. For example, an 11 percent energy loss during the collision between an 8 km/sec oxygen atom and a thermal  $H_2O$  molecule is sufficient to prevent any backscatter. The collision energies are sufficient to excite a number of loss mechanisms, including vibration and rotation or breakage of molecular bonds.

## 4.2 Possible Experiments

The types of experiments considered for space vacuum applications fall into two categories: (1) preparation of ultrapure materials and (2) deposition of thin films on completely degassed substrates.

There is considerable scientific interest in ultrapure metals. Few metals have been purified to better than a few parts per million. It is possible that certain properties could be significantly affected by trace quantities of impurities. For example, the brittleness of Be is atypical of metals. It is conjectured that the small size of the Be ion makes this material particularly susceptible to influences by trace impurities such as oxygen. Vacuum melting and distillation of metals, particularly using containerless techniques, are obvious applications for a space vacuum facility. Earth facilities can achieve the required vacuum levels but have difficulties maintaining these levels with the high heat loads associated with these processes.

Electron transport is another method of purifying metals. An electric current is passed through the sample, heating it to just below melting. The current transports many impurities to the end of the sample, leaving the majority of the material in a highly purified state. This process also requires a very high vacuum to keep gaseous impurities from being incorporated into the sample. In addition to the difficulty of maintaining this vacuum in the presence of the high heat loads, another gravity effect is present. The hot, highly purified metals are extremely soft and deform readily under their own weight.

The primary emphasis in thin film work in high vacuum is to assess the effect that residual gas on the substrate has on the nucleation and growth of crystalline layers. It is hoped that by thoroughly degassing the surface, deposited atoms will grow into large grain size crystals suitable for low-cost, moderately efficient solar cells. Research to date indicates a relationship between grain size and vacuum level in the deposition of Si on W.

## 5.0 Experiments Status and Remaining Issues

### 5.1 Vacuum Environment Definition

There is presently no MPS-supported research in this area.

#### 5.1.1 Remaining Issues

1. What vacuum level can be obtained in the wake of the Shuttle? Where is the optimum location for a space vacuum facility relative to the Shuttle?
2. What is required to develop an adequate model for the wake vacuum? How well can collision cross sections be estimated or measured in a molecular beam facility?
3. What are the best methods for characterizing the vacuum environment and determining the Shuttle outgassing on early Shuttle flights?

#### 5.2 Ultrahigh Vacuum Experiments

No research in this area is currently being sponsored by the MPS program.

##### 5.2.1 Remaining Issues

1. How much support is there for preparation of ultrapure metals? Which metals are of most interest?
2. What vacuum levels can be maintained in conventional vacuum chambers as a function of heat loads? What is the cost of operating such facilities?
3. Is space vacuum operation likely to impact the current solar-voltaic program? Would it have application to a space power station by forming the solar cells in situ?

#### 6.0 Assessments and Recommendations

##### 6.1 Vacuum Environment Definition

One of the first tasks that must be completed is the definition of the Shuttle induced environment and a measurement of the wake vacuum. A first step in this direction will be taken with the Induced Environment Contamination Monitor (IECM). This induced environment monitor contains a sensitive quadrupole mass spectrometer with a collimator to allow directional mapping of the molecular environment at a sensitivity equivalent to  $10^{-13}$  Torr. Its primary objective is to map the emitted flux from the Shuttle by observing the back-scatter of these molecules in the ram direction.

Direct observation of the molecules leaving the Shuttle will also be accomplished using the Remote Manipulator System (RMS) to move the IECM away from the Shuttle. A controlled release of radioactive tagged  $H_2O$  will give a direct measure of the scattering cross section in the forward direction.

Unfortunately, the mass spectrometer on the IECM is designed for detecting molecular species. It uses an antechamber in which the molecules become thermalized to increase their ionization cross section and the instrument sensitivity. This makes it unsuitable for measuring atomic oxygen and hydrogen, which are of primary concern in the wake vacuum applications.

There are various mass spectrometer configurations specifically designed to measure atomic oxygen, and some of them may be available off-the-shelf. It is recommended that the IECM be fitted with such a mass spectrometer and other appropriate diagnostic techniques and used to map the wake environment on an early Shuttle flight. It may very well turn out that the vacuum in the wake of the Shuttle is sufficient to perform most of the tasks envisioned for the space vacuum facility concept. The unique advantage of such a facility is not the extreme vacuum but the ability to reject heat and gas load while maintaining such a vacuum.

## 6.2 Experiment Definition

Consideration should be given to an early demonstration experiment of the space vacuum concept. Depending on the results of the measurements of the modified IECM, such an experiment or experiments could be mounted in or on a self-contained experiment carrier such as IECM or MEA and either hard mounted to a pallet in the Shuttle cargo bay or held away from the cargo bay by the RMS. The most appropriate experiments for such a demonstration would be metal purification, either by vacuum melting, distillation, or electron transport.

Future work in experiment definition should be directed toward defining the limitations of the best vacuum facilities as to their ability to handle high heat loads and gas evolution as well as their cost of operation. These data are needed to run any cost benefit analysis on using an orbiting vacuum facility in lieu of Earth systems.



6.3 Facility Developments Requirements

None is recommended at this time.

6.4 Supporting Research Requirements

A low-level, in-house effort should be maintained to determine the best methods for measuring the wake vacuum and to maintain an awareness of the state of development and possible availability of mass spectrometers that are designed to detect atomic oxygen.

6.5 Working Group Activities

There is not an active working group at present to support the definition of space vacuum requirements. A previous attempt to form such a working group was terminated because of a perceived lack of interest from the scientific community.

A low-level effort should be initiated with selected vacuum experts, including industrial users whose responsibility is the maintenance of high vacuum facilities for production. This group would serve as an indicator of whether a space vacuum facility may eventually be able to compete with Earthborne capabilities.

## BIOPROCESSING

## Bioprocessing

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## Bioprocessing

### 1.0 Introduction

The bioprocessing program is concerned with various biological and biochemical laboratory procedures that might be done more efficiently in the low-gravity environment of space. In particular, four major bioprocessing areas are believed to be significantly hampered by gravity-driven forces such as sedimentation, thermal convection, and concentration-induced convection: (1) separation processes (e.g., electrophoresis and phase partitioning) used in the purification of heterogeneous biological samples; (2) suspension culturing of cells in vitro; (3) crystallization of biological macromolecules for X-ray or neutron diffraction analysis; (4) detailed studies on the rheological properties of blood at low shear rates. For each of these areas, the procedure is first to gain a good understanding of the mechanism's functioning in unit gravity, then attempt to optimize the process for ground-based operation, and utilize space only when the investigator is convinced that the low-g environment offers unique and significant advantages to the bioprocess in question. Specifically, the research efforts so far have centered on an examination of the physical principles underlying electrokinetic processes (electrophoresis, isoelectric focusing, and isotachopheresis). Studies involving cell surface modification, advanced electrokinetic instruments, and the automated electrophoresis device have grown out of this effort. The separation processes laboratory at MSFC is relatively new to the study of phase partitioning methods, but it is expected that a research program of similar scope will evolve in this area as well. Projects in the areas of cell culture, protein crystal growth, and bio-rheology have been proposed but are not now being investigated by NASA. A most important feature of the work is a collaborative effort with the biomedical researchers who will be the eventual users of the technological improvements developed by NASA.

### 2.0 Major Objectives

1. To determine the advantages that might be obtained in the low-gravity environment of space for processing materials of interest to the biomedical community.

2. To design and conduct experiments in space that demonstrate these advantages.

3. To apply the knowledge gained from ground-based and space-based efforts for improving bioprocessing procedures on Earth.

4. To develop strong collaborative interactions with government agencies, private industry, and academic researchers.

5. To identify and explore new techniques of separation or of bioprocessing that might be enhanced by low gravity.

### 3.0 Justification

A number of processes of interest to the biomedical community that are adversely influenced by gravity effects have been identified. These include electrophoresis, isoelectric focusing, phase partitioning, suspension cell culturing, crystallization of macromolecules, and the study of blood rheology. Experiments performed in space can provide valuable insight into the control of the processes on Earth, produce research quantities of unique products, and eventually develop unique separations or products on a preparative scale. A recently signed joint endeavor with an industrial firm is evidence of the potential economic benefits that can come from bioprocessing in space.

### 4.0 Background

There are several facets to the possible application of low-g processing. So far, the primary consideration has been given to separation processes, particularly electrokinetic processes that are affected by convective flows driven by Joule heating of the current passing through the buffer fluid. However, additional applications that deserve careful consideration are also emerging. These will be delineated in the following discussions.

#### 4.1 Separation Processes

Separation of complex material mixtures into their component parts is a goal of extreme importance in many fields but is of particular importance in the various biomedical fields. Indeed, the lack of satisfactory techniques for such separations is now in many cases the

limiting factor that impedes further research progress. The kinds of biological components in need of improved separation methods include the following:

1. Intact living cells: Every organ of the mammalian body is made up of a great variety of functional cell types, which can frequently be best studied in homogeneous populations of a single cell type. However, cells that differ importantly in their functions are often so similar in their size, density, and appearance that it is impossible to obtain a pure population of any one cell type by conventional separation methods (density gradient centrifugation, for example). In addition to facilitating basic research into normal and abnormal cell physiology, improved cell separation methods could conceivably be used to provide purified cell populations for transplantation into individuals lacking normal cells of that type. Also, purified populations of cells that secrete valuable products could be most useful in the commercial production of these substances, because cell culturing processes could be greatly simplified and their efficiency increased by selecting only active, producing cells for culture. A few of the many sorts of cells for which there presently is need of improved separation methods are the following:

The cells of the kidney cortex that produce urokinase, a clot-dissolving enzyme.

The cells of the kidney that produce erythropoietin, a hormone useful in treating certain types of severe anemia.

The insulin-producing beta cells of the pancreatic islet of Langerhans.

The various subpopulations of immunologically active lymphocytes (e.g., T-cells, B-cells, helper cells, killer cells, suppressor cells, null cells, etc.).

The different types of megakaryocytes, the large cells of the bone marrow that give rise to blood platelets.

Separation of malignant from nonmalignant cells of many tissue types.

2. Fragments of cells: In cell biology, there is great interest in studying the activity of certain enzymatic and transport processes that are localized to specific

areas of the cell. Conventional density-dependent separation processes are usually inadequate for isolating from crude cell homogenates the membrane fraction that contains the particular substance of interest; there is evidence, however, that some of the separation techniques being developed in the bioprocessing program are capable of achieving such separations. Similarly, our technology shows promise for the separation of inside-out from outside-out membrane vesicles, an accomplishment that allows researchers to study the activity of molecules normally hidden on the inner surfaces of cell membranes. Another application of subcellular purifications is the preparation of bacterial cell fractions to be used in the manufacture of highly specific vaccines, a field of endeavor that is assuming increasing importance as the disadvantages of indiscriminate antibiotic therapy for infectious diseases become more apparent.

3. **Macromolecules:** Purifying macromolecules that have been synthesized by living cells or laboratory procedures is another application of bioprocessing separations technology. Some macromolecules that have importance because of their clinical usefulness or their research value cannot be synthesized outside the body of a living animal; they must, therefore, be laboriously purified from some extremely heterogeneous medium such as blood, urine, or tissue homogenate. Other valuable macromolecules can be obtained through laboratory procedures, such as cell culture, recombinant-DNA technology, or artificial peptide synthesis. In each of these cases, however, the final product is not a pure solution of the desired substance but, rather, a highly complex mixture with contaminating macromolecules of many types, requiring extensive purification. In addition, neither recombinant-DNA technology nor laboratory peptide synthesis can be performed until the desired product (or its precursor) has been obtained in strictly pure form in sufficient quantity to allow determination of its molecular structure. For many important macromolecules (e.g., interferon, alpha-1-antitrypsin) this has been impossible to achieve in spite of the many techniques presently available for purifying macromolecules. Methods currently employed for the purification of complex mixtures of proteins and other macromolecules include ultracentrifugation, gel filtration, various chromatographic methods (including affinity chromatography, liquid phase chromatography, and high-pressure liquid chromatography), and various electrokinetic methods (usually performed in gels to suppress convection and to provide



some molecular sieving action). None of the above techniques appears to be adversely affected by gravity. However, free-flow electrophoresis, free-flow isoelectric focusing, and phase partitioning could conceivably provide unique advantages over these other techniques if such separations were carried out without the perturbations introduced by Earth's gravity.

In order to establish proper requirements and rationale for developing improved separation processes, the following questions must be addressed:

- What techniques are currently used for cell separation, how successful are they, and what are their shortcomings?
- What applications might improved separation techniques have?
- For what applications have processes that could be improved by use of a low-g environment, such as continuous flow electrophoresis, isoelectric focusing, and phase partitioning, been used in the past?

One important fact to consider in this regard is that most current cell separation techniques are based either on very nonspecific characteristics of the cell (e.g., density) or on characteristics so highly specific that the method can be used only on well-characterized, previously purified populations of cells. For example, to carry out either fluorescence-activated cell sorting (FACS) or immunoaffinity column techniques requires the use of specific antibody to some individual cell surface component. To procure such antibody, a purified cell population must first have been obtained, and the particular cell surface antigen must have been isolated in quantity. Because of these limitations, existing techniques are either quite nonspecific, or else they are "circular" in that it is necessary to possess a purified population before one is able to obtain a purified population. In contrast, both continuous-flow electrophoresis (CFE) and phase partitioning avoid this liability; with either technique, it is theoretically possible to begin with a mixed population of cells about which one knows essentially nothing and to sort them into categories that are specific as well as biologically meaningful. Moreover, both of these methods appear to be significantly impeded by gravity-related effects.

Techniques for accomplishing these separations that could benefit from the low-g environment are described in the following sections.

#### 4.1.1 Electrophoresis

Electrophoresis is a well-known and widely used technique for producing separations of proteins and other macromolecules on an analytical scale. Such molecules acquire a specific charge when immersed in a buffer solution. An applied electric field interacts with the ionic double layer created by this charge and produces a force which moves the molecule against drag encountered in the medium. This allows materials with different mobilities to be separated in either a space or time domain. The surface charge of biological cells is determined largely by glycoproteins associated with the plasma membrane. Importantly, these glycoproteins are not fixed or stereotyped but vary with the cell type and even with the acquisition of specialized functions by certain cells within one cell type. Thus, surface charge is a very appropriate parameter to use in attempting to achieve cell separations that will be biologically meaningful. The electrophoretic mobility of microscopically visible cells or subcellular particles can be measured directly by analytical cell microelectrophoresis. In some instances, the mobility of soluble particles, such as proteins, can be measured if they can be attached to a carrier particle. The established procedures for analytical cell microelectrophoresis are slow and of limited accuracy, and the equipment is difficult to operate with the required precision. Based upon the problems encountered with the method and the established need for mobility measurements, an automated analytical electrophoresis apparatus has been built and is now being tested with different cell populations.

On Earth, electrophoresis is usually carried out in the presence of a gel or other stabilizing medium to prevent convective mixing. This restricts the quantities that can be separated to an analytical scale and also precludes use of the technique for cells, cell components, or clusters of cells. One technique for circumventing this restriction is the use of free column electrophoresis. Column electrophoresis can be performed on Earth by using vertical columns with a density gradient to stabilize the fluid motion; in this system, the cells migrate against gravity. Although this technique has enjoyed only limited

success, it was a first choice for space, where cumbersome and restrictive density gradients are no longer required.

The first experiments, performed as supplementary experiments on Apollo flights, showed that electroosmotic flow at the walls severely perturbed the separation. Special coatings that had a zero zeta potential (i.e., developed no net charge in the presence of the buffer) were developed for the MA-011 static tube electrophoresis experiment flown on ASTP. This experiment was only partially successful but did demonstrate that the electroosmotic flow could be controlled by the use of suitable coatings. Also, there was some indication that kidney cells could be separated according to function. One fraction of cells when cultured showed a significant enhancement in the production of the valuable enzyme urokinase. Column electrophoresis can be a very valuable tool for space use for obtaining extremely high resolution separations of research quantities of material.

Another means of obtaining electrophoretic separation of cells or macromolecules is the use of CFE. By its very nature, free-flow electrophoresis is associated with significant problems, many of which are gravity determined. The passage of the electric current used in a CFE separation causes Joule heating which tends to produce unwanted thermal convection, impairing the resolution of the separation. Other gravity-driven effects, such as sedimentation of the sample material, also restrict the amount of sample-to-buffer density mismatch that can be tolerated, which limits the concentration of the sample and thus the throughput of the technique. The CFE instruments currently in use are stabilized by using a very thin flow channel and moderate buffer flows to suppress buoyancy-induced convective flows. This arrangement limits both throughput (because of the restricted sample stream diameter) and resolution (because the sample stream is subject to distortion from wall effects). Also, such machines have been notoriously difficult to operate with long-term stability because the sample stream tends to drift and meander as a result of minute changes in operating parameters. In addition to the gravity-associated perturbations, nongravity effects, such as wall effects, changes in properties of the fluid, particle-particle interactions, and possibly vehicle-induced accelerations, will also limit the performance of such devices in low-g. In order to determine the benefits that may be obtained by operating in space as well as the most advantageous design

for such devices, it is necessary to understand the fluid dynamics of electrokinetic separations.

Significant effort has been expended in an attempt to understand how wall effects influence the sample stream distortion and to establish the causes for stream meandering. Analytical and computer models have been developed for the thermal field and for perturbations on the Hele-Shaw flow in the chamber. Instrument test chambers have been constructed with multiple thermistors and dye marker ports to measure the thermal and flow fields as a function of buffer flow and power dissipated in the buffer. It has been found that severe stream distortion is produced by circulation patterns that form at Rayleigh numbers as low as 6. Unless the chamber is extremely narrow, such flows result from almost any temperature inversion. Downward-flowing machines are particularly susceptible to this perturbation because heat is being generated in the buffer. The buffer must be brought in warmer than the cooling walls, and more heat must be extracted than is added in order to prevent adverse thermal gradients. This requires a narrow flow chamber which accentuates wall disturbances such as electroosmotic flow and parabolic flow effects. Minimizing such effects requires an extremely small sample stream, which limits the throughput.

Upward-flowing devices can avoid some of the problems and are inherently more stable as far as flow distortions are concerned. However, they are much more susceptible to distortions caused by sample stream density mismatch. Since the sample stream containing cells or macromolecules is usually more dense than the buffer, it tends to fall back as the buffer tries to carry it upward. This, of course, causes severe distortions unless the concentration, hence the density mismatch, is kept very low. Again, this drastically limits the throughput.

It has also been found that such machines are extremely sensitive to any lateral thermal gradients or flow nonconservation, such as would occur from a leak in the electrode chamber membrane. These membranes tend to be somewhat ion selective, which can lead to a pH gradient and uneven heating in the lateral direction. Also, electroosmotic flow tends to move the warmer buffer from the center of the chamber toward the side, which causes lateral temperature gradients.

Most of these difficulties can apparently be avoided in a low-g environment where the buoyant forces would be dramatically lessened. There may be other, non-Boussinesq effects that limit the performance in low-g, but it does appear that there is a good rationale for a flight experiment to explore these effects that are overshadowed by convective problems on the ground.

#### 4.1.2 Isoelectric Focusing

In isoelectric focusing (IEF) a pH gradient is set up by the action of an applied electric field upon ampholytes added to the buffer solution. The material to be separated is driven by the applied field to a region of pH known as the isoelectric point, where the electrophoretic mobility of the sample is zero. The separation achieved is in terms of isoelectric point, and very high resolutions are possible because the boundaries of the sample bands are self-sharpening. This is a particular advantage when dealing with proteins or other macromolecules because the focusing process counteracts diffusion. Being an electrokinetic separation technique, IEF is subject to gravity-induced convection and sedimentation problems similar to those encountered in CFE processes. Like electrophoresis, isoelectric focusing is normally performed within a gel matrix or in a vertical column with a Ficoll or sucrose density gradient to suppress convection arising from the Joule heating. These operating conditions restrict its use to analytical or micro preparative scales. An additional problem with the use of column isoelectric focusing is the tendency of the highly concentrated material focused at the isoelectric point to coalesce into droplets and sediment. Moreover, many proteins form insoluble precipitates at their isoelectric point, a characteristic that disqualifies IEF as a preparative tool in some cases.

A recent proposal by Bier for a continuous-flow IEF instrument that would exploit low gravity to prevent convective mixing was selected for further development. The machine is a recirculating device with a number of fluid loops that come together in a common chamber. In the version constructed for ground-based testing, membranes are used to stabilize the flow in the common chamber. The ampholytes can migrate through the membranes in response to the applied field to form a stepped pH gradient in the various flow channels. Once the pH gradient has stabilized, the sample is introduced and each

component migrates to the channel corresponding to its isoelectric point. A ten-channel machine has been built and demonstrated to be capable of separating a number of test materials. It has been suggested that high-resolution, high-throughput continuous-flow IEF would be a useful method for purifying natural or synthesized products such as polypeptide hormones, interferon, recombinant-DNA products and other macromolecules.

The device has attracted considerable attention in the biomedical community, and a number of researchers have delivered samples to be separated. One major problem impeding this use of IEF comes from the synthetic ampholytes that are used in constructing the pH gradient. It is extremely difficult to remove contaminating ampholytes from the desired final product, and there is much concern that prospective pharmaceutical products would be unacceptable if ampholytes were present. Bier has been working on a system wherein the pH gradient would be formed from mixtures of naturally occurring amino acids rather than commercially synthesized ampholytes. Success in this endeavor would constitute an important advance in the area of IEF purification of molecules. It has also been discovered that often the material to be purified becomes absorbed on the membranes, causing significant fractions of the highly valuable product to be lost. This can be alleviated to some degree, but not eliminated, by an appropriate choice of membrane. It is believed that the membranes could be eliminated entirely by performing the separation in low-g. If this proves feasible, there may be requirements to go to space in order to separate certain extremely valuable pharmaceutical products.

Isoelectric focusing has not been particularly successful in separating cells because the isoelectric point of a cell is usually at such a low pH that it is difficult to maintain cell viability. Cell clumping in IEF columns causes sedimentation. Also, the ampholytes are apparently toxic to many cells. Studies in our laboratory have shown that pH gradients could be established in buffers without the use of ampholytes. A citrate buffer was found to be particularly well suited to isoelectric focusing of cells. Viability can be maintained even with low pH if the time of exposure is short. Isoelectric focusing of cells on Bier's machine may be made possible by modifying or removing the membranes separating the flow chambers. Working with Professor Righetti (University of Milan, Italy), it has been possible also to perform

isoelectric focusing on the Hannig FF-48 continuous-flow electrophoresis apparatus. These advances open exciting new prospects for cell separation based on a property different from conventional electrophoresis. Again, the use of a low-g environment may be required in order to operate the Bier recirculating device without the flow-stabilizing membranes or to achieve the full potential of the continuous-flow electrophoresis device.

#### 4.1.3 Phase Partitioning

Phase partitioning involves separating cells or macromolecules according to their different interfacial energies into two immiscible aqueous polymeric solutions, such as dextran and polyethylene glycol (PEG). In phase partitioning the sample is shaken with the two fluids, and the system is allowed to settle, with the heavier dextran coming to occupy the lower portion of the vessel. Depending upon its surface properties (e.g., surface charge or membrane lipid composition), the sample will tend to associate itself either with the upper phase, the lower phase, or the fluid-fluid interface. (In cell separations, the partitioning is usually between the upper phase and the interface.) Separation is accomplished by decanting. When a long series of mixing and decantation steps is used, the procedure is called countercurrent distribution (CCD). Phase partitioning has been shown to be capable of separating erythrocytes of different mammalian species, human erythrocytes of different ages (a separation impossible to achieve electrokinetically), intestinal epithelial cells with different secretory functions, and various subcellular organelles. The aqueous polymeric solutions are quite compatible with cell viability. Some experiments have indicated that it may be possible to alter selectively the partitioning behavior of certain types of cells by attaching to the PEG phase affinity ligands that bind to specific receptor sites on a given cell type. This possibility makes phase partitioning a potentially powerful and highly specific cell separation technique. However, gravity effects can interfere significantly with CCD separations. For example, cells suspended in the lighter phase tend to settle toward the interface while the system is equilibrating. Indeed, it is not possible to allow an Earthbound partitioning experiment to proceed to equilibrium because at equilibrium all cells will have sedimented to the interface. Also, concentrations must be restricted to prevent cell aggregation and clumping at the interface with the rapid sedimentation

of cell clumps through the interface. It has been suggested that separations carried out in low-g could avoid such sedimentation, thus enhancing resolution significantly. A substantial increase in surface area could be obtained by maintaining a fine dispersion of one phase in the other. This should greatly aid in establishing equilibrium conditions and obtaining a complete separation. Of course, some mechanism must be found for separating the two phases in the absence of gravity without affecting the distribution of cells.

A phase partitioning separation system called the toroidal coil chromatograph (TCC) was developed at the National Institutes of Health (NIH) and has been acquired by MSFC. The proposed research program using this instrument involves evaluating its capabilities, optimizing its performance with test particles (for comparison with a projected space experiment), and developing a wider array of polymers to be used in constructing the two phases. Such polymers should have greater flexibility and broader applications than the currently available dextran-PEG pair. In addition, the TCC will be used in an attempt to fractionate bone marrow samples provided by the Hematology Division of the Center for Disease Control for the purpose of obtaining purified populations of megakaryocytes, the bone marrow cells that give rise to blood platelets.

#### 4.2 Cell Culturing and Characterization

Cells, because they are living organisms, demand much more care in handling than do nonliving biological materials such as macromolecules. In order to utilize the separation schemes discussed in the previous section, elaborate techniques must be worked out for extracting a cell mixture from a living organism, preparing it for separation, placing the cells on a production culture after separation, assaying for production of the desired products, and finally harvesting the product. All of this must be done while maintaining sterility and viability.

##### 4.2.1 Cell Cultures to Support Space Separations

The early space experiments on cell separation utilized a freeze-thaw technique for transporting cells to space for separation and for return to Earth for production culturing. This technique was only marginally suited for such purposes because of the small fraction of cells that survived the two freeze-thaw cycles. Better methods



are mandatory for any cell separation in space on a preparative scale. Some improvements appear possible. For example, it is known that certain additives such as DMSO can enhance the viability during a freeze-thaw cycle. This was not allowed on ASTP because of crew safety considerations. Other approaches might be to transport and maintain the cells in culture. It may eventually be desirable to also perform the production culture in space and return only the harvested product.

#### 4.2.2 Suspension Cultures for Increased Yield

It has been suggested that the space environment may offer certain advantages for maintaining cultured cells in suspension. In particular, it is pointed out that in the absence of gravity, a suspension culture would require no agitation because the cells would have no tendency to sediment to the bottom of the vessel as they do on Earth. It is suggested that eliminating the need for agitation might enhance the viability of the cultured cells because they would not be exposed to the high shear rates and liquid-gas interfaces that are generated by spinner agitation techniques. Many types of cells that are commonly grown in culture form a sheet, or monolayer, on the bottom of the culture flask. These cells have an absolute requirement for attachment to a surface and will not grow in suspension culture. However, recently developed techniques for growing such cell types on the outer surface of dextran beads, or on the inner surface of microcapsules, may provide a means of growing attached cells in suspension, a process that would probably magnify the capacity of a given culture system enormously. In this case, the advantages of microgravity for suspension cell culture are worth careful study.

There are, of course, some obvious difficulties of maintaining suspension cultures in weightlessness. Unless there is some convective stirring, the only mechanism for supplying nutrients and removing waste products is diffusion. This is a highly inefficient process and it may be difficult to maintain a viable culture under complete diffusion-controlled conditions. There are some advantages to the introduction of a small amount of convective mixing (the small residual vehicular accelerations may be sufficient) to overcome this problem while retaining the postulated advantages of performing suspension culturing in low-g.

#### 4.2.3 Cell Harvesting

One of the limiting factors in harvesting useful products from cell cultures is the length of time the production culture can be maintained. First, the cells themselves have limited lifetimes and die in the production culture. The culture can be maintained through several generations by placing some of the cells on a growth culture which allows them to reproduce and multiply. However, with normal cells this process is limited. Cells can be transformed with viruses and made virtually immortal, but the products from such cells may not be suitable for pharmaceutical uses.

An even more serious limitation is the tendency for many cells to lose their ability to produce their particular product after only a few generations. This is not well understood.

The problems are not peculiar to low-g processes but are fundamental to all cell culturing applications. They must be kept in mind in the development of any space application. For example, if it proves to be possible to separate unique cell lines in space for production culturing, it will be necessary to perform the separation process repeatedly to maintain a fresh supply of cells for the production process.

#### 4.2.4 Cell Characterization

Another problem in cell separation is the spread in mobilities among supposedly homogeneous populations. Unlike nonliving materials, not all cells of a similar nature have exactly the same structure. The surface proteins can change for a variety of reasons, such as variations in mitotic cycle, response to hormones or antigens, and the general health of the cells. A major concern in the use of cell electrophoresis is whether the intrinsic spread in electrophoretic mobilities from the preceding effects might produce spreads greater than the resolution required to obtain a good separation from the mixture of cells.

Techniques have been developed to obtain an extremely homogeneous population of different cell lines that differ by only a small mobility change. Measurements are being made of the intrinsic spread in mobilities for these groups of cells that are as homogeneous as current

preparation permits. These will serve as excellent models to evaluate various separation processes and will determine the maximum usable resolution for electrophoretic separators.

#### 4.2.5 Cell Surface Modification

The practical utility of electrokinetic cell separations is limited by the fact that functionally distinct cell subpopulations sometimes overlap in their electrophoretic mobility distributions, making a clean separation impossible. In such cases, it would be valuable to be able to alter selectively the electrophoretic mobility of one subpopulation of interest, making it separable from the other elements of the sample. Recent work done under contract has shown that the mobility of fixed human erythrocytes can be reduced by 40 percent by attaching to their surfaces a large number of microspheres made of poly (gluteraldehyde) or poly (vinylpyridine), polymers which have zero electric charge at physiological pH. The microspheres are attached to the cell surface by coupling them to a specific antibody or lectin that has an affinity for the target cells. This procedure was shown to make possible the separation of human from turkey erythrocytes, in spite of the fact that these two populations normally differ in their electrophoretic mobilities by only 3.7 percent, too small an amount to allow their preparative separation. This procedure may prove useful in facilitating low-g separations of important cell subpopulations. However, it has the drawback of requiring specific antibody to the target cell for attachment of the microspheres, and few of the target cell populations of greatest interest have ever been obtained in sufficient purity and quantity to allow the preparation of specific cell-surface antibody. Furthermore, the methods commonly used in removing microspheres from cells after the separation is complete are frequently incompatible with cell viability.

#### 4.2.6 Droplet Arrays

The possibility of constructing containerless droplet arrays in space is another potentially useful tool for cell culture in microgravity. As visualized by Dr. Jacobus of the STAMPS committee, such containerless droplet arrays could be deployed and manipulated by acoustic or electrostatic forces in a three-dimensional grid, allowing the isolation of individual cells or clones in

specialized environments. This capability would make it possible to study factors influencing cell viability and to set up ideal environments for generating clones of mutant cells. The idea has not been actively pursued because no prospective user has expressed an interest.

Another possible application of such an array might be suspension culturing. The large surface to volume ratio afforded by the small droplets could facilitate rapid exchange of gases at the interface and may alleviate some of the difficulties mentioned previously in maintaining suspension cultures in space. At present this concept is not being actively considered.

#### 4.3 Crystallization of Biological Macromolecules

The study at the atomic level of the structure of various proteins and other biological materials is extremely important in understanding their function. The primary tool used today for such studies is X-ray diffraction, but this technique cannot easily determine the positions of hydrogen atoms in the structure of the molecule. To obtain that kind of information, neutron diffraction must be performed, but neutron diffraction requires much larger crystals, some millimeters in diameter. Single crystals of this size are difficult to grow from the materials of interest. It has been shown that the largest attainable size of a protein crystal is inversely proportional to its rate of growth. It has been suggested that proteins crystallized in the diffusion-controlled, low-g environment of space might grow so slowly that they would become large enough for neutron diffraction analysis. Furthermore, it is speculated that proteins that cannot be crystallized for X-ray diffraction studies on Earth because of their molecular complexity (e.g., ribosomes, nucleosomes, and complex enzymes such as pyruvate dehydrogenase) might become crystallizable in space because in the absence of sedimentation effects the very large nucleation sites these molecules form would be able to maintain the proper orientation for crystal formation.

Crystallization of biomolecules has received little attention from the crystal growth community, having traditionally been the province of biochemistry. It would be valuable to bring together these two areas of expertise,

permitting state-of-the-art technologies for inorganic crystal growth to be applied to the problems of growing biomolecular crystals. Extensive ground-based work is a prerequisite for any development in this area. In particular, a thorough study of the various factors that affect nucleation and growth rates of these crystals should be carried out before any flight experiments are planned or undertaken.

#### 4.4 Blood Rheology

Blood is a non-Newtonian fluid with a viscosity that is strongly dependent on shear rate, particularly at very low shear rates. This fact is due primarily to the presence of the erythrocytes, which make up slightly less than one-half of the total volume of fluid. The rheology picture is further complicated by the fact that erythrocytes form aggregates, or rouleaux, of varying sizes in different physiological conditions. At low Reynolds number flows, coagulation or flocculation may occur with concomitant rapid sedimentation of colloidal aggregates. Rheological considerations appear to be important in several disease states, including cardiovascular disease, diabetes, sickle-cell anemia, and some forms of kidney disease. For example, sedimentation of red blood cells is more pronounced in a variety of pathological conditions and forms the basis for the in vitro test of erythrocyte sedimentation rate. The rapid sedimentation of the red cells arises from their aggregation and rapidly results in a very low anisotropic system which precludes precise rheological examination under zero or low flow conditions. Does the enhanced cellular aggregation in pathological conditions in vivo produce a different pressure drop across a blood vessel? Simultaneous erythrocyte sedimentation precludes an answer to this question. An increase in the pressure drop might merit appropriate countermeasures, whereas a decreased pressure drop would constitute a beneficial situation not requiring therapeutic intervention. Obtaining a thorough understanding of the rheology of blood is extremely difficult. The examination of biological cellular dispersions in cone-in-plate or coaxial cylinder viscometers at low rates of shear would be a useful space experiment to investigate the cell-cell interactions and their contribution to viscosity without interference from sedimentation.

## **5.0      Experiment Status and Remaining Issues**

### **5.1      Bioseparation**

#### **5.1.1    Electrophoresis**

##### **5.1.1.1 Bioseparations Technology (Snyder)**

The major thrust of this effort is to develop a detailed understanding of the role of gravity in various bioprocessing methods, with most of the emphasis placed on CFE. In particular, the objectives are to determine the limiting performance imposed by gravity on various devices, determine whether there is a potential improvement to be realized by performing such separations in space, and determine whether increased understanding of the fluid flow could lead to improvements in ground-based separations.

Several test flow chambers have been constructed with thermal and flow diagnostics to study the various flow stabilities that arise from buoyancy and sedimentation effects. Insight into the causes of sample stream meandering, flow distortions, membrane effects, and other flow anomalies has been obtained from such studies. Experiments performed in the chambers have been compared with theoretical models developed by Saville (Princeton University) and Rhodes (MSFC). It has been shown that ultimate operating limits on such systems are set by heat transfer considerations at the faces of the chamber. These limitations hold whether the machine is operated in down-flow or up-flow configuration or in low-g. Moreover, flow disruptions from these limitations occur in conventional CFE devices with transparent chambers at power levels lower than those required to produce the transverse distortions predicted earlier by Ostrach. This recognition and other considerations has led to a new concept in CFE design that should produce a significant improvement in ground as well as space operation.

In addition, the principal causes of sample stream meandering and lack of long-term stability under normal operating conditions have been identified as flow nonconservation effects, such as leaks in electrode membranes, or lateral thermal nonuniformities. These arise from heat transport in the electrode regions, from ionic selectivity of the membranes, and from electroosmotic flow transporting the cooler buffer flow near the cooling

wall into the center of the chamber near one electrode. Most of these effects should diminish significantly in low-g. A space experiment is being developed to explore any remaining nongravity-driven flows that might still persist.

A state-of-the-art bioseparation laboratory has been established at MSFC featuring the best available techniques under consideration for use in space. The devices available include a Beckman CFE machine, a Hannig FF-48 CFE machine, LKB column electrophoresis and isoelectric focusing devices, a TCC (developed by Ito at NIH), two Rank capillary microscopic electrophoretic machines for analytical electrophoretic mobility measurements, and a new computer-automated analytical electrophoretic machine (developed by Bartels, University of Arizona). The purpose of this laboratory is to explore the limitation of the devices when operated on the ground, to provide prospective users with the best available separation techniques for testing various candidate materials to determine if proposed space separations are feasible, and to provide a basis for comparison between separations accomplished in space with the best available ground-based techniques. Improvements obtained from the fluid dynamical studies discussed previously will be incorporated into these facilities. A new CFE concept has been developed by Rhodes, and a device is being constructed for evaluation.

Another important aspect of cell separation being explored is how specificity and resolution of various separation techniques might be affected by variations in the genetic makeup, mitotic cycle, history, or nutritional status of the cells to be fractionated. For example, if cells in different mitotic stages should prove to have markedly different electrophoretic mobilities (or partition coefficients), it may be necessary to mitotically synchronize a cell population before attempting to separate it into subfractions. To address this question, we are attempting to obtain well-characterized homogeneous cell populations that are mitotically synchronized and to determine the mobility spread of these cells by analytical electrophoresis. Having once determined the minimum irreducible spread for a homogeneous population, a second population, differing slightly in cell surface markers, will then be investigated. This study should determine whether it is possible to separate cells on the basis of

known surface properties and should set an upper limit on the resolution that can be effectively utilized in cell separation.

In addition, it is of great value to demonstrate that physical properties of the cell surface (as measured by electrophoresis or phase partitioning) are actually correlated with important functional characteristics of the cell, such as the ability to secrete a certain hormone. Separation of heterogeneous cell mixtures into functionally distinct subpopulations by electrokinetic or partitioning methods has already been demonstrated to be feasible for a limited number of cell types, but these correlations have not yet been documented extensively enough to become accepted as a general rule. For this reason, each new demonstration that functionally specific cells (e.g., pancreatic beta cells, renal urokinase-secreting cells) have characteristic electrophoretic mobilities or partition coefficients is of significant value to the program.

#### 5.1.1.2 Study of Continuous-Flow Electrophoresis in Space (Richman)

This effort, sponsored partially by the MPS program and largely by McDonnell Douglas Astronautics Company (MDAC), was devoted to exploring the potential advantages of performing CFE separations in space. Detailed numerical procedures were developed to evaluate the flow profiles in a CFE chamber, and experimental systems have been constructed and operated. Of particular importance has been the exploration of up-flow configurations, use of extended length columns, and effects of density mismatch between buffer and sample.

These efforts have led to a joint endeavor between NASA, MDAC, and a major pharmaceutical company. Under the terms of this endeavor, MDAC will design and build a CFE electrophoretic separator to be flown on an early Spacelab flight and will eventually use the device to produce commercial products. This represents the achievement of a major goal in the MPS program; i.e., to encourage organizations in industry to utilize space for their own purposes. Technical support in the form of research results from the Government-sponsored research will be made available to MDAC to assist in their design of the device. MDAC, in turn, will provide results of



separations on standard particles supplied by the Government to demonstrate the effectiveness of the separation.

#### 5.1.1.3 MA-011 Reflight

At present there are no MPS-sponsored flight experiments approved for the Shuttle. A joint MSFC/Johnson Space Center (JSC) in-house effort is under way to refurbish and refly the MA-011 apparatus on an early Shuttle flight. A primary emphasis will be on repeating the kidney cell experiment that produced the provocative results on ASTP. In addition, several runs will be made with well-calibrated standard particles to evaluate the resolution of the technique and to explore the limits imposed on concentration by particle-particle interactions. This latter effect is of particular importance to future low-g applications because the absence of sedimentation may allow the use of much higher concentrations than are possible in normal gravity.

#### 5.1.1.4 Automated Electrophoresis Analyzer Apparatus (Bartels)

The Automated Electrophoresis Analyzer has been completed and is now undergoing operational tests at the University of Arizona. NIH has funded the construction of a second system with minor modifications.

The present device will remain at the University of Arizona for completion of the operational tests, which are providing some unique electrophoretic mobility data that will result in several publications. In addition, the kidney cells to be flown on the MA-011 reflight are being measured in the Automated Electrophoresis Analyzer; when these tests are completed in mid-summer 1980, MSFC will take delivery of the system.

#### 5.1.2 Isoelectric Focusing

##### 5.1.2.1 Development of a Recirculating Isoelectric Focusing Separator (Bier)

A ten-channel recirculating isoelectric focusing (RIEF) separator has been developed and is operating routinely. An automated data acquisition system monitors the pH in each channel and the progress of the separation. A number of heterogeneous samples have been separated.

The resolution compares favorably with analytical isoelectric focusing in gels, but the materials can now be separated on a preparative scale.

Two shortcomings have been identified with the laboratory machine. First, the ampholytes required to produce the pH gradient contaminate the sample. These would be unacceptable for any pharmaceutical use of the separated material. Work is progressing on finding a substitute for the ampholytes that could either be readily separated from the sample or that would be unobjectionable if not separated. Second, the membranes cause some problems. Many materials of interest tend to adhere to the membranes and form coatings. This reduces the efficiency of the separation and can result in a significant loss. This can be a serious problem, considering the high values of some of the materials being separated. Also, the electroosmotic pressure produced by the membrane affects the flow in the system.

Elimination of the RIEF's flow-straightening membranes is thus a highly desirable goal. To approach this issue, it is proposed to build a membraneless model of the RIEF and operate it on the ground, both with and without the electrical current that is necessary for performing separations. If it is found that laminar flow can be maintained on the ground only in the absence of electrical current (and therefore the absence of Joule-induced thermal convection), then there would be a strong rationale for attempting actual IEF separations on a membraneless machine in low-g.

### 5.1.3 Phase Partitioning

#### 5.1.3.1 Countercurrent Distribution of Biological Cells (Brooks)

D. E. Brooks (University of Oregon Health Sciences Center) is the principal investigator of a funded effort designed to develop a field-driven system for phase separation in low-g. Since in reduced gravity the two polymer phases will not separate via density-driven settling, an alternate method is being developed utilizing an electric field rather than a gravitational field. In some systems drops of one phase suspended in the other exhibit an electrophoretic mobility that increases linearly with drop diameter. It is this characteristic which allows an applied electric field to drive phase separation.

Brooks has developed phase systems that maintain cell viability and have high phase drop mobilities, and he has demonstrated electric field-driven separation in these phase systems.

#### 5.1.3.2 New Polymeric Solutions for Phase Partitioning (Harris)

A recent effort has been initiated with Dr. Harris (UAH Chemistry Department) to develop a broad spectrum of immiscible polymeric solutions for use in phase partitioning separations. The materials should increase the flexibility and selectivity of the phase partitioning, which presently utilizes PEG-dextran.

In conjunction with this effort a TCC designed by Dr. Yoichiro Ito (NIH) has been obtained through cooperative agreement with NIH and MSFC. Several outstanding biomedical scientists have expressed interest in undertaking collaborative investigations using the TCC. Specifically, the contemplated separation projects include purification of bone marrow megakaryocytes (with B. L. Evatt, of the Center for Disease Control), purification of pituitary somatographs (with Wes Hymer of (Pennsylvania State University)), separation of pancreatic islet cell types (with Art Charles of University of California, Irvine), and isolation of enzyme-bearing membrane vesicles (with G. Sachs of University of Alabama in Birmingham). This membrane will provide hands-on experience with phase partitioning techniques and will be used to explore the limitations of this process in Earth's gravity. Such knowledge is essential to design a meaningful space experiment

#### 5.1.4 Remaining Issues

The remaining issues in electrophoretic separation are:

- Theoretical performance assessments for available electrophoretic separation devices should be computed using the work of Rhodes and Saville and compared with measured performance using well-characterized standard particles.

- Similar expected performance should be computed for an optimized Earth-based CFE and for an optimized space-based CFE to assess the potential benefits of performing such separations in space and to evaluate the performance of such machines when they become available.

- Better standard particles are required. The spread in mobility of currently available standard particles is only slightly smaller than the resolution of the best available CFE machine. Therefore, it is difficult to differentiate between intrinsic mobility spread of the standard and the distortions produced by the machine.

- Perhaps the most important question concerning the future of free-flow electrophoresis is whether improvements in resolution will result in biologically useful separations, or does the inherent spread in homogeneous samples already exceed the existing machine resolution for most materials of interest. Corollary questions are: what causes this spread in mobilities in a homogeneous population and can it be controlled by mitotic synchronization or other means?

- Sterilization of devices such as CFE machines is extremely difficult, especially when the entire machine cannot be autoclaved. Special difficulties are encountered when the machine contains a number of different materials, some of which are incompatible with various germicides.

- Consideration should be given to utilization of such devices for nonbiological materials for which there is large commercial interest, such as paper fibers. Improved performance of ground-based separators would be of enormous practical importance to many industries.

Many of the remaining issues identified for electrophoresis also apply to other separation techniques. Specific issues relating to isoelectric focusing are:

- The limiting resolution on Bier's RIEF machine should be established and its ability to separate subtly differing macromolecules in a complex mixture demonstrated. In particular, the purification of significantly prepared pharmaceuticals should be demonstrated.

- A detailed comparison should be made of the RIEF technique and other competing separator techniques for macromolecules, including affinity chromatography, high-pressure liquid chromatography (HPLC), and ultracentrifugation.

- The use of the RIEF technique for cell separator should be explored. Can membranes with sufficiently large pore size to allow passage of cells be used and

still be effective flow straighteners? Would this be a possible space application? Would the citrate buffer developed by Boltz at MSFC be suitable for this use?

- Operation of the RIEF without membranes should be explored on the ground in an isothermal zero-power test to determine if there are inherent reasons why such a scheme would not work in space. An early space experiment is required to demonstrate the membraneless operation with power.

- Does the elimination of membranes completely solve the problem of absorption of samples, or would the sample also tend to coat other parts of the device?

- Operational limits should be established for other isoelectric focusing devices, such as the Hannig FF-48 operated with a pH gradient in the buffer or the LKB column electrofocusing device.

The issues to be resolved in phase partitioning are:

- The separations currently possible in one-g must be established.

- The limitations imposed by gravity must be analyzed and their origin understood.

- The specificity of the technique using PEG-dextran and other polymer solutions under development must be determined. Methods for improving the specificity should be explored, either by using additives to one or the other phases, or by use of affinity ligands to couple one of the solution components to receptor sites on the macromolecule to be separated.

- The separation of the immiscible phases in space deserves careful consideration. Brooks has given considerable attention to the use of electrophoresis. However, there may be simpler methods, such as low-level centrifugation or any of the mechanisms that operate in the separation of monotectic alloys.

## 5.2 Cell Culturing and Characterization

### 5.2.1 Cell Culture in Support of Space Separators

#### 5.2.1.1 Biosynthesis Laboratory (Morrison)

The biosynthesis laboratory has monolayer and suspension cell culture capabilities. Current research includes procedures for obtaining cell cultures, growing and maintaining continuous cell cultures, and freezing and storing cells. A continuous line of baby hamster kidney (BHK) cells has been grown in suspension, and the growth of cells on microcarriers is being pursued. A variety of beads were used as substrates for the attachment of cells, and good results have been obtained with BHK cells. Procedures for the analysis of biochemicals produced by cell cultures have been established. Fibrinolytic and colorimetric methods are being used routinely for the assay of urokinase. The production of urokinase in monolayers of human embryonic kidney cells and the biochemical purification of secreted products on affinity columns are being developed. Procedures for the chromosome analysis of cell cultures (counting and karyotyping) have been established. A laboratory model of a bioreactor for the continuous automated growth of cells in suspension will soon be operational, and data collection of cells in suspension will be initiated. Studies will continue on the growth of human kidney cells in suspension, and ground-based technology for the growth of cell cultures in suspension will be evaluated to optimize cell culture growth and product synthesis.

#### 5.2.1.2 Kidney Cell Electrophoresis (Todd)

The reflight of the electrophoresis technology experiment has required additional research into suitable buffer systems with cryoprotective agents to increase the viability of the kidney cells after multiple freeze-thaw cycles and evaluation techniques to determine the separation of kidney cells according to function.

The electrophoretic separation of kidney cells has been strongly dependent on the source and preparation of the kidney cells. Separations have been done by density gradient electrophoresis that show multiple peaks, and experiments are under way to measure urokinase production by the different fractions.

#### 5.2.1.3 Purification and Cultivation of Human Pituitary Growth Hormone-Secreting Cells (Hymer)

Wesley C. Hymer at Pennsylvania State University is exploring various approaches to the problem of using

cultured pituitary tissue as a source of human growth hormone. Separation technology is important to this effort for the purposes of isolating somatographs (the growth hormone-secreting cells) from other pituitary cell types, separating out those somatographs having the highest production capability, and eliminating extraneous cells that might interfere with the performance of the cultured or implanted somatographs. Hymer's group, working in conjunction with Paul Todd, has obtained promising results with density gradient electrophoresis and continues to pursue this line of research. In addition, arrangements have been made for a sample of Hymer's pituitary tissue to be fractionated on Ito's phase partitioning device (the TCC) at MSFC during the summer of 1980.

#### 5.2.2 Suspension Cell Culturing in Low-g

##### 5.2.2.1 Suspension Cell Culturing in Space (Mieszkuc)

These studies are designed to (1) obtain data on the performance of cell culture vessel system elements and to define the biological oxidation process--the transfer of oxygen from gas to liquid and from liquid to oxidant--and (2) determine the limits of ground-based technology using a preprototype reactor or studying enzymatic reactions and suspension cell cultures. The enzymatic conversion of glucose into gluconic acid is being used as a model to test the interactions between dissolved oxygen, glucose oxidase and glucose to determine the correlation between on-line operating sensors and the course of reaction in this particular bioreactor. Signals originating from the dissolved oxygen probe give information on the rate of reaction and the rate of oxygen transfer into the liquid water under different experimental conditions. A computer model has been developed which can correlate theoretical and experimental data and which can be adopted for on-line, real-time monitoring of bioprocesses performed simultaneously under terrestrial and microgravity conditions.

Current efforts include: replicate experiments to achieve high statistical accuracy of the sensor performance, the development and construction of a space bioreactor prototype, experimental testing of the prototype space bioreactor, and a project plan for the ground-based research to be completed before a flight experiment can be flown in a Shuttle/Spacelab mission. Follow-on efforts are expected to include the design, construction, verification testing, and flight test of a small space bioreactor

to demonstrate the concepts and limitations of these new techniques using mammalian cells in culture which produce compounds of scientific or commercial importance.

#### 5.2.2.2 Plant Cell Culture in Low-g (Sharma)

The basic tenet of this work is that plant cells may be more suitable for culturing in the space environment than animal cells, primarily because of the less stringent requirements for growing plant cells in vitro. Greater success has been attained in understanding the aspects of growth, development and differentiation with plant cells than with animal tissue; thus the system may permit more precise study of the specific influence of the space environment (particularly weightlessness) on these growth processes. Agronomically important cereals (rye, Durum wheat, and triticale) were selected for ground-based studies of cell culturing to confront problems encountered in their culturing and the utility of weightlessness in solving these problems.

#### 5.2.3 Cell Surface Modification

##### 5.2.3.1 Electrophoresis Cell Separation Based on Immunomicrospheres (Rembaum)

In an attempt to make electrophoretic separations more specific, a technique for decorating the cells with microspheres coated with antigens is being designed to react with specific receptor sites on the cell type to be separated. The microspheres alter the mobility of the cells to make them easily separable electrophoretically.

The techniques for preparing the cells have been developed, and modification of the cell mobilities has been demonstrated. There are still difficulties, however. One of the problems is the removal of the microspheres without damaging the cell. A major problem with any separation based on immunotagging is the development of the antisera required to prepare immunological coupling between the desired receptor and the tag. This generally requires that one start with a clean homogeneous population of the cells.

Finally, in the work on cell surface modification, several questions remain:



- Is it possible to remove the immunomicrospheres without damaging the cells?

- Is it necessary to remove the immunomicrospheres, or can the cell be put on growth culture with the spheres attached?

- Assuming a satisfactory solution to the problem of what to do with the attached immunomicrospheres is found, the question of application remains. Presumably the enhanced throughput made possible by space electrophoresis could be put to good advantage by extracting a tagged population from a complex mixture on a truly preparative scale. However, there may be other, simpler techniques, such as incorporating a ferromagnetic component into the microspheres and using magnetic separation methods.

#### 5.2.4 Remaining Issues

Better methods are clearly required for transporting cells to and from orbit while maintaining viability. Freezing the cell probably represents the simplest solution to this problem provided that procedures can be developed for enhancing viability through the freeze-thaw cycles.

Transporting the cells in culture may be desirable. One concern in the use of suspension cultures is the response of the system to launch accelerations. If cells are transported in monolayer cultures, they must be removed, placed in suspension, and inserted into the separator on orbit.

The advantages of culturing cells in low-g have never been clearly established, theoretically or experimentally. Large-scale suspension cultures are, in fact, operated on the ground. There may be some gain in cell viability if stirring could be eliminated, but some stirring is necessary to transport nutrients and remove waste products. The issue is whether a reduction in stirring could be expected to result in improved yield.

One of the applications envisioned for cell separation involves purifying a cellular subpopulation according to function and culturing the cells that produce a specific desired product. However, nonmalignant cells generally grow well in culture for limited periods only; they frequently stop producing their products even before

the culture dies out. This situation raises many questions that should be addressed:

- What progress can be made in overcoming the lifespan problem through medium supplementation with growth factors?

- Can the productivity of a short-term culture be significantly enhanced by selecting and culturing high-producing subpopulations?

- Are there ways to render the products of malignant cell lines sufficiently innocuous to be approved for human pharmaceutical use:

- How likely is it that alternative techniques such as recombinant DNA or laboratory molecular synthesis will succeed in producing the desired cell product?

- What role might NASA separations technology play in these alternative processes?

### 5.3 Crystallization of Macromolecules

There is presently no MPS-sponsored work in this area.

#### 5.3.1 Remaining Issues

The central issue is to determine if the quiescent environment of space offers any advantage in the growth of macromolecular crystals. To answer this question, a detailed review of current growth techniques should be undertaken to determine the limiting factors imposed by gravity. In addition, novel techniques applicable only in low-g should be explored, such as the use of a cooled string to maintain local saturation in a diffusion-controlled growth process.

### 5.4 Blood Rheology

There is presently no MPS-sponsored work in this area.

#### 5.4.1 Remaining Issues

Several leading researchers in blood rheology have expressed an interest in performing experiments in a

low-g environment. The major issue is to determine the most meaningful experiments and how they might be implemented.

#### 6.0 Program Assessment and Recommendations

The separation and purification of macromolecules, cells, and cell components are major problems in biomedicine and are likely to remain so for the foreseeable future. In addition, other major biological research areas (e.g., rheology, protein crystal growth, cell culture) may benefit significantly from NASA-developed technology. The techniques and materials of interest will, of course, vary depending on the progress that is made, but improvements in processes can always be expected to yield exciting results. However, the field is vast and rapidly moving. Therefore, it is imperative for NASA to develop close ties with the workers who need improved bioprocessing techniques.

In spite of the potential benefits of utilizing low-g in a variety of bioprocessing activities, we find ourselves in the peculiar posture of having no approved MPS-sponsored flight experiments under development for early Shuttle flights. The MPS 5-year plan calls for a new start to develop a bioprocessing module in 1982, which dictates that 1986 would be the earliest possible time that any substantial results could be obtained. This also requires that we identify the requirements for such a module and build a solid constituency of users by 1981. There are several difficulties with this:

1. We have not demonstrated to the biomedical community that substantial improvements can be expected from the utilization of low gravity. In fact, we have not yet clearly identified which processes can be improved or shown how much improvement can be expected by space processing.

2. Given the rapid advancements in biomedical fields, it is difficult to anticipate which technologies will be important in 1986. Therefore, it is difficult to identify meaningful requirements with the level of detail required to initiate a new start in the time frame directed by NASA's operating procedure. These difficulties are accentuated by the lack of any definitive results on which to build.

3. It is difficult to generate much enthusiasm in the biomedical community for advances in technology that will not be realized for 6 or 7 years. In order to develop a meaningful partnership, we must be in a position to offer returns from our technology on a more immediate basis.

In order to be prepared to initiate a new start in FY 1982, the following must be accomplished:

1. A strong partnership with selected elements of the biomedical community must be established on a quid pro quo basis--NASA supplying its expertise in developing basic understanding of both terrestrial and space processes of interest to the biomedical community which, in turn, keeps NASA informed of its need and requirements and the progress being made in the fields of mutual interest.

2. NASA must establish its expertise in being able to develop a fundamental understanding of the various processes and show how they are affected and limited by gravity. It must demonstrate how this understanding may be put to use on the ground by developing improvements in the existing technology, and the expected improvements achievable in low-g must be clearly defined in a scientifically defensible manner.

3. It must be demonstrated that such improvements are, indeed, achievable in the spacecraft environment and that effects that are often masked in Earth's gravity do not dominate and interfere with the intended process in space. Also, various assumptions made about certain aspects of the process in space must be tested and verified. This will involve a certain amount of flight experimentation.

4. Most of the processes being considered for use in space are not widely used or understood by the biomedical community. This is almost axiomatic. If the process is widely used on Earth, it is generally not severely limited by gravity effects; hence there is little benefit to be gained by going to space. NASA, therefore, not only has the job of selling the concept of using space to improve such processes, it must also convince the user community that the process in question will be effective in solving some of the identified problems.

## 6.1 Electrophoresis

Although there are many facets to the bioprocessing program, electrophoresis is by far the most developed in terms of rationale and technique. Several flight experiments have already been accomplished; and although they were not unqualified successes, much was learned, and the feasibility of electrophoresis in space was clearly demonstrated. The STAMPS committee strongly recommended that future experiments be directed toward demonstrating that space offers an advantage in the separation process rather than toward the production of any particular pharmaceutical product.

Fluid dynamics and other process studies have, therefore, received the majority of recent attention. An extensive theoretical and experimental program to investigate flow phenomena and gravity-related disturbances in electrophoresis chambers has been initiated and is now beginning to yield exciting results. When this program has been completed and its results documented in the scientific literature, we must then use these results to determine the maximum theoretical performance obtainable with the best ground-based electrophoresis separators. Standardized procedures for measuring the performance must be developed to characterize the various machines and to compare their performance against their theoretical limit. Performance limits for machines operating in low-g must be estimated in order to show the expected gain by going to space. Confirmation of this expected increase in performance using the same characterization techniques developed for laboratory machines will be an important goal of the early Shuttle experiments.

Concurrent with this, we must maintain close liaison with the user community in order to coordinate our efforts with their research needs. Literature searches and personal contacts in the field have revealed that CFE is more widely used in Europe than in the U.S. (This is due largely to the efforts of Dr. Kurt Hannig and his colleagues at the Max Planck Institute for Biochemistry, Munich, who developed the machines and pioneered their use.) Based on the results of these studies, we believe there are many potential advantages of CFE in terms of maintaining cell viability and function, especially when large numbers of cells are required.

We must therefore work closely with the biomedical community on establishing the applicability of this technique and making researchers aware of the potential improvement in performance that can be obtained in space. This can best be done by establishing and maintaining state-of-the-art cell separation capabilities and encouraging leading researchers in the biomedical sciences to supply samples to be separated. By the use of analytical electrophoresis, we can establish whether there is sufficient difference in the mobilities of two populations to hope to obtain a separation. By the use of existing continuous-flow machines, we can establish whether there is some hope of separating the cells by function. This will determine whether or not the prospective user can expect to benefit from the higher performance of space electrophoresis.

The other applications of low-g processing may become more important than electrophoresis in the long run, but they are not as mature at this time. The limitations of terrestrial techniques have not been clearly established nor have the potential advantages of low-g processing been elucidated. These aspects should receive the major emphasis in developing the newer concepts.

#### 6.1.1 Relationship with Industrial Joint Endeavors

There is active interest from several privately funded organizations to build and operate electrophoresis and possibly other separation devices in space through NASA's recently announced Joint Endeavor Program; and, in fact, one industry has already signed such an agreement. This type of operation is one of the primary goals of the NASA MPS program; i.e., to develop the concepts of utilizing low-gravity processes to the point that privately funded corporations will want to continue such operations for their own use.

The early NASA emphasis on the development of electrophoresis will provide the basic proofs of concept needed to solidify such a joint venture between the Government and industry. The long-term relationship is less clear at this time because of the uniqueness of this way of doing business. However, since the emphasis of such an agreement can be expected to focus on production of pharmaceuticals on a commercial scale, it appears that there will be a continuous role for the Government to promote the development of bioprocessing in space for research purposes for the following reasons:

1. The quantities of materials required for research purposes are generally so small that there is little or no profit motive for a commercial firm to become involved.

2. The government has little or no control over the capabilities of facilities developed by a commercial firm. These will be chosen to meet the customer's needs and may not be optimum for the production of research quantities of materials.

3. It would be inappropriate for one Government agency to be forced to negotiate with a private industry for use of a Government-subsidized facility for the purpose of carrying out research.

4. There is always the danger that the industries involved will find the operation unprofitable and drop out of the program. We believe that the potential societal benefits of developing improved biomedical processes in space are too great to accept this risk.

Therefore, it appears that the Government should continue to pursue an active program to develop bioprocessing in space with the emphasis on meeting the needs of the biomedical research community. This would be complementary to any program developed by private industry that would be geared to the needs of the pharmaceutical industry.

#### 6.1.2 Innovations in Electrophoresis

The unique environment provided by space offers the opportunity to utilize innovative approaches to electrophoresis that cannot be performed on Earth. An effort should be made to stimulate some bold new ideas rather than simply improving existing techniques.

For example, one of the factors that makes gel electrophoresis an extremely useful tool for analytical work with mixtures of proteins is the ability to separate according to molecular weight (or, more accurately, according to molecular size which is related to molecular weight) by taking advantage of the sieving effect of the gel substrate. Generally, such techniques are not useful for preparative work because of the small quantities involved and because of the difficulty of extracting the proteins from the gel. Nor are they useful for cells

because the pores of the gels that can be produced on Earth are too small.

A variant of electrophoresis that has been neglected on the Earth is transient field or pulsed electrophoresis. In this method, a series of short pulses is applied to the sample instead of maintaining a d.c. field across the separation column. The amount of separation is not influenced by the transient response which is dependent on the mass of the sample in addition to its charge and drag. This adds a new dimension to the properties that can be addressed by the separation process. In addition, the applied wave form can be made asymmetrical with high-voltage, short pulses of one polarity and with much longer, low-voltage pulses of the opposite polarity. The molecules in the buffer are generally much lighter than the sample, and those near a wall will tend to move virtually instantaneously in response to the applied wave form. If the net wave form is made to average to zero, these molecules have no net motion, and electroosmotic flow is virtually eliminated. The sample, on the other hand, cannot respond as rapidly as the buffer molecules; therefore, the sample motion depends on its mass as well as its charge and drag.

One difficulty with this approach is that net motion is a second-order effect and is much smaller than would be obtained by a straight d.c. machine. This is a problem on the ground where the separation time is limited by flow and other considerations. In space, however, the virtual absence of gravity-induced sedimentation and convection allows the added time required for the separation.

A novel method for dealing with wall-induced flow distortions in electrophoresis utilizes a moving wall technique. Such a device has recently been designed at MSFC. A patent application has been filed, and a working model is being constructed. In such a system, the buffer and sample are carried along between two endless belts that form the moving walls so that there is no flow relative to these moving walls. Electrode chambers are located at the edge of the belts to provide the field. Electroosmosis is controlled by coating the belts with a low zeta-potential coating or by the transient field technique discussed in the previous paragraph. Since there is no flow to help stabilize against convection, terrestrial use requires that the gap between the two moving walls be made extremely narrow. However, since there are no wall



distortions, the sample can occupy the entire thickness of the gap between the moving walls. In space this gap, hence the throughput, can be increased substantially.

Multidimensional separations offer considerable promise in analytic work. The O'Farrell technique has been used for a number of years for diagnostic and other analytic purposes using gel electrophoresis in one direction and sodium dodecyl sulfate (SDS) gel electrophoresis in the other. The SDS alters the charge on the functional groups and essentially causes separation according to molecular weight. Righetti (University of Milan) has recently shown remarkable results by performing electrophoresis in one direction and isoelectric focusing in the other. Both of these techniques require the use of gels for stability and are therefore, restricted to macromolecules. In space, such separations could be performed in free-flow systems or in large pore size gels and, thus, be applicable to cells.

It was mentioned previously that the use of gels aided in the separation of macromolecules because of their sieving action. It has not been possible to prepare gels with pore size sufficient for use with cells. In the absence of hydrostatic pressure and convective flow, it may be possible to form large porous gel structures that could be used with cells.

## 6.2 Isoelectric Focusing

The progress being made by Dr. Bier in the development of a continuous-flow isoelectric focusing device has been most gratifying. The ground-based work serves two essential purposes: (1) establishing the technique as a new separation process and developing a group of potential users, and (2) identifying limitations imposed by gravity on the performance of the device, thus establishing the rationale for going to space to obtain improved performance.

To assist in meeting these objectives, a duplicate of the prototype or an improved second generation machine should be located in the Separation Processes Branch at MSFC for evaluation and to help develop a constituency of users. Also, it is recommended that a flow visualization mock-up be developed for studying the convection effects with and without membranes. This could lead into a flight experiment or demonstration to determine the amount of cross-channel mixing in low-g.

### 6.3 Phase Partitioning Separations

The existing program at the University of Oregon (Brooks) and the MSFC in-house program (Harris) should determine the limitations of Earth-based processing and establish the benefits that one can expect to obtain in space. A demonstration experiment should be considered for an early Shuttle mission, whether as a self-contained carry-on experiment (such as MISE) or an experiment on the FES to take advantage of the elaborate optical system.

### 6.4 Cell Culturing and Characterization

The development of an array of standard particles and the ability to determine rapidly and accurately the mobility distribution of a statistically significant number of cells are major accomplishments in the field of electrophoresis. This allows us to characterize various separation processes and to determine whether a heterogeneous population of cells has separable components. It also tells us the resolution needed to perform the separation.

Determination of the minimum irreducible mobility spread of a homogeneous cell population is also of major importance to the application of electrophoresis. This spread may very well limit the application of cell electrophoresis. If, for example, the inherent spread of mobilities is comparable to present CFE resolutions, there is very little to be gained by increasing resolution unless methods can be found to reduce the spread by mitotic synchronization or surface modification.

Likewise, the question of whether it is possible to maintain cells in culture in order to harvest a product must be answered before wholesale separation of cells for this purpose can become a reality. Methods for sterilizing the Beckman CFE are being developed at MSFC, and cells that can form culture can now be separated.

One of the outstanding questions remaining from the ASTP MA-011 experiment is whether the kidney cells that produce urokinase could be separated on the ground. Hannig has succeeded in separating renin-producing cells from kidney tissue but has not attempted to assay the resulting fractions for urokinase production. This issue must be settled before the MA-011 reflight is made. A joint effort between MSFC and JSC will address this problem.

## 6.5 Crystallization of Macromolecules

This is a recently recognized application that has a very high potential for a significant scientific payoff. Some supporting research should be initiated on this topic as soon as possible. Dr. Ed Meehan (UAH) is active in this field and would serve as a local expert to help develop a program along these lines. We should find means to involve Dr. Meehan in this program.

## 6.6 Blood Rheology

Several meetings with Dr. Giles Cokelet and his coworkers have resulted in a letter of intent to propose a blood rheology experiment for the FES.

## 6.7 Required Supporting Research and Technology

In addition to the research activities described earlier, there are some supporting efforts required from other disciplines to complete the various bioprocessing tasks. Specifically:

1. Study of convection phenomena in systems with stabilizing thermal gradients and/or flows. The literature abounds with papers dealing with unstable convection under static conditions or natural convection driven by transverse density gradients only. But what happens when there are stabilizing vertical gradients and/or impressed flows that are comparable to the convective flow? This is precisely the situation in a CFE chamber, and it has never been properly analyzed.

2. A model for particle concentration effects. Macromolecules or small cells that are sufficiently dilute form suspensions subject to Brownian motion and Stokes law. However, in a concentrated solution, they behave collectively and act as a fluid with a different density. What is the critical concentration corresponding to the crossover between individual and collective behavior? What determines this critical concentration? How do concentration effects alter the response of the particle to an applied field? These problems are being studied by Dr. Omenyi, an NRC visiting scientist at MSFC.

## 6.8 Available Flight Hardware and Flight Opportunities

Since some flight experimentation is required to test assumptions, prove concepts, and demonstrate expected improvements in low-g processing, the planning must be keyed to available early flight opportunities and to hardware that could be available to meet these flight schedules.

The hardware that could be useful for such a demonstration experiment is:

1. The MA-011 column electrophoresis unit that was flown on ASTP is being refurbished for reflight. Although this reflight is not being sponsored by the MPS program, it does provide the opportunity to test several concepts and to demonstrate that resolution improvements can be obtained in low-g. At present the emphasis is on repeating the ASTP kidney cell experiment, although two samples will be used to determine the maximum resolution and assess the importance of concentration effects in band spreading. Two samples are woefully inadequate for this effort, and these necessary diagnostics should be expanded.

2. The SPAR-E continuous-flow electrophoresis chamber was configured as a SPAR experiment early in the program. The available time on SPAR is too short to do a meaningful experiment, but the apparatus with minor modifications could be flown on the MEA; the chamber is presently configured for collection and does not have flow visualization capability. It would be useful in its present form for demonstrating stability at higher operating powers than can be used on the ground but would not be able to provide diagnostic details on any flow instabilities should they develop. Extensive modifications would be required to provide such capability, and it is not clear that such modifications are compatible with the present design and packaging.

3. The Fluids Experiment System. The sophisticated optical system being developed for the FES would be useful for investigating various flows and fluid processes. However, it will not be flown before late 1983 and is already committed to other experiments on that flight. The earliest anticipated use for a bioprocessing experiment in the FES will not be flown before late 1984. Also, an experiment specific test cell would have to be

designed and fabricated to accommodate whatever experiment was identified. Although such experiments would be highly desirable, they would come too late to satisfy the requirement for data in time to support an FY 1983 new start on the bioprocessing module.

4. A variety of relatively simple "suitcase" experiments could be designed to fit into the mid-flight deck and be operated by the crew on early Orbital Flight Test (OFT) flights. This offers the only opportunity to test any concepts other than electrophoresis experiments. To support flights in the FY 82 time frame, apparatus definition must be completed by late 1980.

#### 6.9 Required Working Group Activity

An essential ingredient of the bioprocessing program is a close working relationship with scientists in the leading medical research centers, pharmaceutical companies, and at the NIH in order to:

1. Identify the significant classes of problems that may be aided by processing in low-g.
2. Identify desired improvements in Earth-based processes.
3. Help guide our work and assure that it is relevant to real needs and has not been superseded by the rapid advances in the field.
4. Develop a cadre of potential users of bioprocessing in space.

This task will provide broad support for all aspects of the program and will provide the interface between the NASA program and the user community.

The bioprocessing program has maintained close working relationships with various members of the biomedical community for a number of years through the Universities Space Research Association (USRA) bioprocessing committee. Recently this effort has been supplemented by a working group of interested biomedical scientists from various medical schools and the NIH. Initially the emphasis was on electrokinetic techniques for separation of cells and proteins or other macromolecules. Additional areas of interest have now been identified, including

multidimensional electrokinetic separation, phase partitioning separation, unique suspension cell culturing techniques, the growth of macromolecular single crystals for neutron diffraction analysis, and the study of blood rheology. Extensive analyses have been done on various materials that require improved separation techniques. The analyses reveal that extensive improvements are needed in both cell and protein separation techniques. In particular, there appear to be many applications for improved cell separation techniques, especially for research purposes. It is difficult to specify exactly the applications space separation processes will find when they become available because of the rapid advances in the field. However, it does appear that the possible improvements that can be attained in low-g will continue to be of interest to the biomedical community. For this reason it is mandatory that close coordination be maintained with leading workers in the field in order to keep abreast of their requirements.

APPROVAL

MATERIALS PROCESSING IN SPACE — 1980 SCIENCE  
PLANNING DOCUMENT

By Robert J. Naumann

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

  
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